

GCA-EoS: A SAFT group contribution model—Extension to mixtures containing aromatic hydrocarbons and associating compounds

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ABSTRACT

GCA-EoS is the first equation of state that takes into account association using a SAFT-like group contribution term. It has been recently upgraded to deal simultaneously with multiple associating and solvating groups. In this work a review of applications and parameters revisions are presented and the GCA-EoS extension to aromatic hydrocarbons is discussed. These compounds are important in different industrial fields (textile, fine chemicals, pharmaceutical, petrochemicals, materials, etc.). Moreover, compounds like phenol play a major role not only in several polymers syntheses but also in biomass processing mixtures. Specifically, the extension to systems containing aromatic hydrocarbons (BETX and alkylbenzenes), water and alkanols is discussed.

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1. Introduction

The Group Contribution (GC) with Association Equation of State (GCA-EoS) is the first EoS of the SAFT family [1] that uses a GC approach of the Wertheim model [2,3]. By assuming a value of one for the radial distribution function, it was possible to take into account the association contribution by a GC approach. In this way a single set of associating parameters of a given group can be applied to the corresponding homologue family of organic compounds independently of the alkyl chain. Therefore the extension of the model to multicomponent mixtures is greatly simplified. Moreover, it reduces the number of equations to be solved in order to find each group non-associated fractions, which is a time demanding procedure.

Aromatic compounds are present in a great deal of industrial applications. They play a major role in chemical synthesis and pharmaceutical processes due to their high reactivity. Moreover, these compounds and their derivatives are used not only as raw material for chemical synthesis but also as solvents. They are important chemicals in polymers that are essential in the textile industry like polyester and nylon. In addition, the growing interest in biofuels and biorefineries design call for the development of thermodynamic tools able to predict phase equilibria in multicomponent-associating mixtures containing aromatic hydrocarbons.

The binary systems alkyl-aromatic compounds+water have been studied by several authors using the SAFT-type association contribution. Suresh and Elliot [4] were the first to evaluate the impact of water self-association model with two, three or four associating sites (2B, 3B or 4C) on the liquid–liquid phase behavior using ESD-EoS. Even though solvation between aromatic rings and water has been demonstrated with spectroscopic data [5], the authors did not consider cross-association between these compounds claiming that they wanted to reduce the number of fitting parameters. Good correlations were achieved with ESD for benzene, xylene and ethylbenzene at temperatures higher than 350 K. No information is given about ESD-EoS capabilities between the freezing point and this temperature. Folas et al. [6] and Oliveira et al. [7] applied CPA to model various binary mixtures. Both works achieved excellent correlation of the water solubility in the hydrocarbon phase; however, CPA seems to fail in describing adequately the temperature dependence of the hydrocarbon solubility in the water phase. On the other hand, Tsivintzelis et al. [8] evaluated the performance of sPC-SAFT and NRHB to model the binaries water+benzene and water+ethylbenzene. NRHB achieves a better correlation of the mutual solubility than sPC-SAFT, even though it shows some divergence at higher temperatures. Like CPA, both models show an important deviation in the temperature dependence of the hydrocarbon solubility in water. Given the fact that the solubility of water in hydrocarbons is important for many industrial applications, in general more attention is given to predictions in the hydrocarbon phase than in the aqueous phase [7–9]. However, this is not the case when hydrocarbon losses in an aqueous solutions need to be well predicted (for example in alkanolamine [10] or glycol aqueous

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Table 1
Original GCA-EoS applications to processes design and optimization.

	Cross assoc available with. . .
Self-associating groups and application	
OH group for H ₂ O, alcohols and phenols (2B)	
Alcohol dehydration	[17,18,21–24]
Water-hydrocarbon immiscibility prediction	[25]
Hydrogenolysis of vegetable oils	[26,27]
Biodiesel processing	OH–COO [28–31]
Water–DMSO cosolvents for supercritical extraction	OH–DMSO [32]
Phase equilibrium engineering of supercritical reactors	[27,28,31,33,34]
COOH (1A)	
Vegetable oils and derivatives processing	COOH–OH, COOH–COO [19,35,36]
Aromatic compounds processing	COOH–OH [37]
Review of associating mixtures: acids, esters, ketones, alcohols processing	COOH with COO, OH OH with COO, CO [20]
Non-Associating mixtures	
Removal of chemicals from fatty oils	[38]
Supercritical fluid fractionation of fish oil	[39,40]
Hydrogenation of vegetable oils	[26,27,41]
Hydroformylation of 1-hexene	[34]
Prediction of double retrograde vaporization:	[42]
Supercritical fluid extraction and fractionation	[40,43,44]
Mixed solvents design for vegetable oil extraction	[45,46]
Extraction of Allium oils from garlic and onion	[47]

Table 2
GCA-EoS revised parameterization for multiple associating and solvating groups.

Associating mixtures	Cross assoc available with. . .
H ₂ O (4C) and OH (2B)	
Alcohols, water and hydrocarbons (linear and branched) mixtures	H ₂ O–OH [14,15]
Biorefineries and Biofuel blends (ethanol + naphtha)	H ₂ O–OH [14–16] and this work
NH ₂ , NH, N (1A)	
Alkylamines with hydrocarbon, water and alcohol	NH _x –OH, NH _x –H ₂ O [10,50]
Natural gas processing (alkanolamines)	NH _x –OH, NH _x –H ₂ O [10]
Aromatic ring (1A)	
BETX and alkylaromatic compounds, water, alcohols mixture	AR–H ₂ O, AR–OH (this work)

AR: aromatic ring.

Table 3
Associating and solvating groups available in GCA-EoS.

	H ₂ O ^a (4C)	OH ^a (2B)	COOH (A1)	COO (A1)	AR ^a (A1)	NH ₂ ^a (A1)	NH ^a (A1)	N ^a (A1)	CO (A1)	DMSO (A1)
H ₂ O ^a (4C)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OH ^a (2B)		✓	✓	✓	✓	✓	✓	✓	✓	X
COOH (A1)			✓	✓	X	X	X	X	X	X

^a Revised parameters for global phase diagrams, AR: aromatic ring. A1, 2B and 4C: one, two and four assorting site, respectively.

solutions) or in environmental applications. For biomass processing, predictions of the aqueous phase compositions are required, while for biofuels the composition of the hydrocarbon phase is needed. Therefore, we made a global minimization of deviations in both phases, in order to develop a robust model for exploratory purposes. In the studies with CPA, sPC-SAFT and NRHB, respectively, the authors considered a weak solvation of the water molecules with the π -electrons of the aromatic ring. In order to account for this effect, cross-association between a proton-acceptor site in the

aromatic ring and proton-donor sites in the water molecule was taken into account. In this way the three models were able to properly correlate water solubility in hydrocarbon but only a qualitative description of the hydrocarbon solubility in water (there is an important deviation in the temperature dependence of this solubility). In the case of GCA-EoS including this solvation allows accurate fitting of the mutual solubility in the complete temperature range.

Regarding alkanols + aromatic hydrocarbons, Folas et al. [6] correlated data of methanol and ethanol with benzene and toluene

Table 4
GCA-EoS pure-group energy parameters for the attractive term.

<i>i</i>	<i>q_i</i>	<i>T_i[*]</i>	<i>g_i[*]</i>	<i>g_i[']</i>	<i>g_i^{''}</i>	Reference
CH ₃	0.848	600	316,910	–0.9274	0	Skjold-Jørgensen [51]
CH ₂	0.540	600	356,080	–0.8755	0	Skjold-Jørgensen [51]
CHCH ₃	1.076	600	303,749	–0.876	0	Soria et al. [15]
ACH/AC	0.400/0.285	600	723,210	–0.606	0	Skjold-Jørgensen [51]
ACCH ₃ /ACCH ₂	0.968/0.660	600	506,290	–0.8013	0	Skjold-Jørgensen [51]
CH ₃ OH	1.432	512	547,425	–0.6195	0.2488	Soria et al. [14]
C ₂ H ₅ OH	1.972	514	438,929	–0.6945	0.1448	Soria et al. [14]
H ₂ O	0.866	647.1	964,720	–1.2379	1.0084	Soria et al. [14]

Table 5
GCA-EoS binary energy interaction parameters for the attractive term.

Group		k_{ij}^*	k'_{ij}	α_{ij}	α_{ji}	Source
<i>i</i>	<i>j</i>					
CH ₃ /CH ₂ /CHCH ₃	ACH	1.041	0.0944	0.3915	0.3915	Skjold-Jørgensen [51]
	ACCH ₃ /ACCH ₂ /ACCH	0.975	0	0	0	Skjold-Jørgensen [51]
H ₂ O	CH ₃ [∞]	0.75	-0.15	0	0.5	Soria et al. [14]
	CH ₂ [∞]	0.76	-0.15	0	2.4	Soria et al. [14]
	CHCH ₃ [∞]	0.89	-0.15	0	0.3	Soria et al. [15]
	CH ₃	1.01	0.06	2	0	Soria et al. [14]
	CH ₂	1.04	0.06	2	0	Soria et al. [14]
	CHCH ₃	1.00	0.05	1	0	Soria et al. [15]
	ACH [∞]	0.91	-0.056	2	4	LLE benzene + water
	ACCH ₃ [∞]	1.04	0	0	0	LLE <i>m</i> -xylene + water
	ACCH ₂ [∞]	1.15	0	0	0	LLE ethylbenzene + water
	ACH	0.95	-0.0869	6	0	VLE water + benzene and LLE water + ethanol + benzene
CH ₃ OH	ACCH ₃	1	-0.072	3	9	VLE water + toluene and LLE water + ethanol + toluene
	CH ₃	0.91	-0.05	1	3	Soria et al. [14]
	CH ₂	0.98	-0.05	3	6	Soria et al. [14]
	ACH	0.952	-0.05	0.1	0.2	VLE benzene + methanol
C ₂ H ₅ OH	ACCH ₃ /ACCH ₂	1.01	0	1	0	VLE <i>p</i> -xylene + methanol
	CH ₃	0.92	-0.05	4	3	Soria et al. [14]
	CH ₂	0.99	-0.05	3	0	Soria et al. [14]
	ACH	0.957	-0.05	0.1	0.1	VLE benzene + ethanol and LLE water + ethanol + benzene
CH ₂ OH	ACCH ₃ /ACCH ₂	1	0	1	0	VLE <i>p</i> -xylene + ethanol and LLE water + ethanol + toluene
	CH ₃	0.895	-0.09	0	0	Soria et al. [14]
	CH ₂	1.020	0.005	0	0	Soria et al. [14]
	CHCH ₃	0.942	-0.10	0	0	Soria et al. [14]
	ACH	0.96	0	0	0	VLE benzene + 1-propanol
	ACCH ₃ /ACCH ₂ /ACCH	1.04	0	2	0	VLE <i>p</i> -xylene + 1-propanol, toluene and <i>p</i> -xylene + butanol

Table 6
Cross-association parameters.

Group		$\epsilon_{ij} k_B^{-1}$ (K)	κ_{ij} (cm ³ mol ⁻¹)	Source
<i>i</i>	<i>j</i>			
H ₂ O	H ₂ O	2350	0.3787	Soria et al. [14]
	OH	2833	0.2576	Soria et al. [14]
	AR	1760	0.230	LLE benzene-water
OH	OH	2759	0.8709	Soria et al. [14]
	AR	1740	0.300	VLE benzene-methanol and benzene-ethanol

AR: aromatic ring.

using CPA, while Grenner et al. [11,12] studied binary mixtures containing BETX with alkanols (ethanol up to nonanol) using sPC-SAFT and NRHB model. Folas et al. [6] also evaluated CPA performance to predict methanol and ethanol distribution coefficients between water and aromatic hydrocarbon, they showed that CPA is able to describe qualitatively the phase behavior. About the cross-association between the alcohol group and the aromatic ring, using FTIR spectroscopy, Brinkley and Gupta [13] found clear evidence of the formation of H-bonds between the alcohol and the aromatic molecules. Folas et al. [6] and Grenner et al. [11] neglected

this interaction; however, they claimed that this solvation might become important to be considered at low temperatures and/or dilute solutions. Later, Grenner et al. [12] did take into account this cross-association in the binary ethanol + benzene. In our case, since we are interested to apply the GCA-EoS over a broad temperature and composition range, we take this solvation into account.

In this work the extension of GCA-EoS to systems containing BTEX, alkylbenzenes, water and alcohols is presented. The initial goal of this work was to develop a model able to predict phase behavior of fuel/biofuel blends. In that respect, a review of the

Table 7
BETX and alkyl benzenes vapor pressure prediction.

Compound	T_r	P (kPa)	T_c (K)	d_c (cm mol ⁻¹)	ΔP (%)
Benzene	0.48–0.97	3–4080	562.0	4.3861	4.1
Toluene	0.48–0.97	2–3400	592.0	4.7702	3.1
<i>o</i> -Xylene	0.50–0.97	2–3110	630.3	5.0726	4.5
<i>m</i> -Xylene	0.50–0.97	2–2930	617.0	5.1108	2.7
<i>p</i> -Xylene	0.50–0.97	2–2960	616.2	5.1163	3
Ethylbenzene	0.50–0.97	2–2990	617.1	4.998	3.9
1,2,3-Trimethylbenzene	0.51–0.95	2–2376	665.0	5.3372	5.9
1,2,4-Trimethylbenzene	0.51–0.96	2–2410	649.0	5.3898	3.9
1,3,5-Trimethylbenzene	0.51–0.98	2–2550	637.0	5.4276	2.2
<i>n</i> -Propylbenzene	0.51–0.97	2–2660	638.3	5.3007	4.1
<i>i</i> -Propylbenzene	0.51–0.97	2–2510	631.0	5.2647	5.1
<i>m</i> -Diethylbenzene	0.52–0.96	2–2080	663.0	5.5264	6.5
<i>n</i> -Butylbenzene	0.52–0.98	2–2090	660.5	5.5620	3.5

Table 8
GCA-EoS correlation and prediction of water + aromatic hydrocarbon binary systems.

Hydrocarbon	T (K)	P (kPa)	Δx_{HC}		Δx_W		N	Ref.
			AAD	ARD%	AAD	ARD%		
Correlation								
Benzene	273–553	30–9500	1.3E–04	7	4.6E–03	11	114	[53,54]
<i>m</i> -Xylene	273–544	101–8000	8.5E–05	9.8	2.5E–02	56	36	[53]
Ethylbenzene	273–510	10–10680	2.10E–05	20	1.50E–02	21	74	[53,55,56]
Prediction								
Toluene	273–548	101–8600	1.5E–03	11	3.1E–02	29	139	[53,54,57]
<i>o</i> -Xylene	273–318	101	1.1E–05	33	4.9E–04	27	9	[53]
<i>p</i> -Xylene	273–555	2.4–10000	2.7E–05	18	1.2E–02	34	46	[53,54,58]
1,2,3-Trimethylbenzene	288–318	101	6.8E–06	64	–	–	4	[53]
1,2,4-Trimethylbenzene	288–319	101	1.9E–06	22	–	–	4	[53]
1,3,5-Trimethylbenzene	288–373	101	2.2E–06	16	6.3E–03	70	21	[53]
<i>n</i> -Propylbenzene	273–359	101	3.5E–06	37	–	–	15	[53]
<i>i</i> -Propylbenzene	288–353	101	1.0E–05	69	2.6E–04	7	21	[53]
<i>n</i> -Butylbenzene	280–373	101	2.30E–06	66	–	–	18	[53]
<i>m</i> -Diethylbenzene	310–582	101–11700	2.3E–04	38	9.6E–02	55	6	[59]

Table 9
Comparison between GCA-EoS, ESD [4], CPA [6], NRHB [8] and sPC-SAFT [8] models accuracy for the binary systems water + aromatic hydrocarbons.

HC	T (K)	$\Delta x_{HC} \% / \Delta x_W \%$							Full T (K) range	GCA all data sets
		ESD 2B	ESD 3B	CPA	NRHB	sPC-SAFT	GCA			
Benzene	313–473	9.7/17	13/15	–	–	–	7/12	273–553	7/11	
	273–473	–	–	19/5.3	–	–	7/13			
	280–540	–	–	–	17/3.6	18/18	8.5/15			
Toluene	273–473	–	–	23/5.1	–	–	9.1/31 ^a	273–548	11/29	
Ethyl-benzene	368–536	27/30	20/24	–	–	–	35/31	273–510	20/21	
	303–568	–	–	47/6.5	–	–	16/23			
	280–540	–	–	–	17/3.6	18/18	30/30			
<i>m</i> -Xylene	398–473	18/17	23/37	–	–	–	9.5/95	273–544	9.8/56	
	373–473	–	–	8.3/3.7	–	–	8.6/97			

^a GCA-EoS prediction.

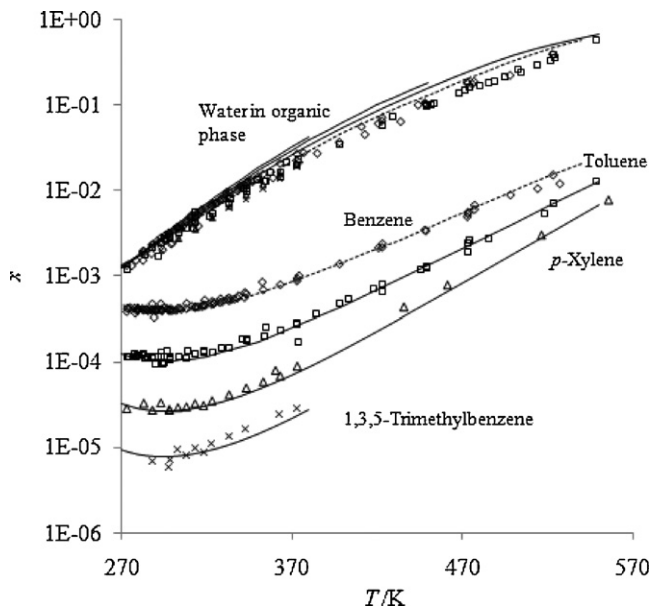


Fig. 1. Mutual solubilities of benzene and methylaromatic hydrocarbons with water. Experimental data [53,54,57,58]: (\diamond) benzene, (\square) toluene, (Δ) *p*-xylene and (\times) 1,3,5-trimethylbenzene. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS predictions.

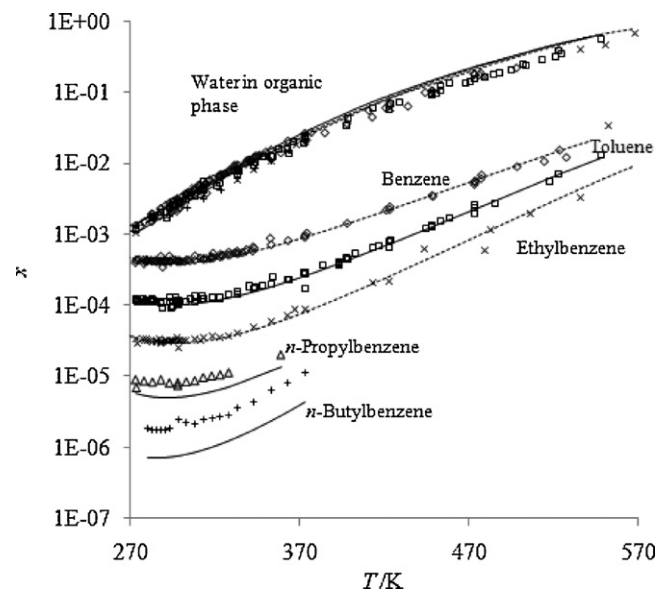


Fig. 2. Mutual solubilities of alkylaromatic hydrocarbons with water. Experimental data [53–57]: (\diamond) benzene, (\square) toluene, (\times) ethylbenzene, (Δ) *n*-propylbenzene and (+) *n*-butylbenzene. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS predictions.

Table 10
GCA-EoS correlation and prediction of alcohol + aromatic hydrocarbon binary systems.

Compounds		T (K)	P (kPa)	$\Delta Z\%$ ^a	$\Delta y_1\%$	N	Ref.
1	2						
Correlation							
Methanol	Benzene	313	24–49	2.8 ^P	38	75	[62]
		326–311	45	0.12 ^T	4.6	25	[63]
Ethanol	<i>p</i> -Xylene	313	3–35	4.3 ^P	2.2	42	[62]
	Benzene	313	24–33	1.5 ^P	2.3	24	[62]
		341–351	101	0.07 ^T	–	11	[64]
1-Propanol	<i>p</i> -Xylene	313	3–18	3.8 ^P	5.1	32	[62]
	Benzene	318	7–26	0.6 ^P	2.3	11	[65]
		350–370	101	0.16 ^T	6.2	7	[66]
1-Butanol	<i>p</i> -Xylene	313	3–8	0.95 ^P	1.2	17	[62]
	Toluene	373	64–86	2.3 ^P	1.7	9	[67]
	<i>p</i> -Xylene	313	2–4	1.6 ^P	3.6	11	[62]
Prediction							
Methanol	Benzene	293–493	10–417	1.6 ^P	3.9	92	[68–74]
		353–303	31–101	0.27 ^T	21	88	[63,75–78]
	Toluene	313	8–37	4.1 ^P	13	42	[62]
		336–384	101	0.4 ^T	13	141	[79–83]
		337–411	101	0.22 ^T	1.2	13	[84]
Ethanol	Ethylbenzene	337–409	101	0.15 ^T	0.9	13	[84]
	Benzene	318,323	27–51	1.8 ^P	2.7	35	[85–87]
		305–408	24–446	0.1 ^T	5.6	51	[86,88,89]
	Toluene	313	8–18	3.4 ^P	35	40	[62]
	<i>p</i> -Xylene	351–411	101	0.3 ^T	2.9	26	[90,91]
1-Propanol	Ethylbenzene	351–409	101	0.5 ^T	7.0	25	[91,92]
	Benzene	313–348	7–90	1.5 ^P	6.8	44	[62,93–95]
		Toluene	313	7–11	1.1 ^P	1.7	
2-Methyl-1-propanol	<i>p</i> -Xylene	370–411	101	0.17 ^T	1.3	23	[96]
	Benzene	350–402	101–253	0.3 ^T	8.3	112	[97]
		Toluene	333–353	15–50	1.4 ^P	16	45
1-Butanol	Benzene	298–318	1–30	1.4 ^P	0.4	26	[62,65,99]
		350–423	91–293	0.2 ^T	6.4	85	[100–103]
	Toluene	313,363	3–63	1.2 ^P	1.9	35	[62,104]
1-Pentanol	Benzene	340–391	27–101	0.16 ^T	2.8	86	[67,105–107]
		396–391	101	0.11 ^T	2.2	23	[107]
	Toluene	313	1–25	3.0 ^P	–	24	[95]
		303–383	1–100	3.5 ^P	2.8	100	[108]
Ethylbenzene	402–411	101	0.2 ^T	5.2	15	[107]	

Superscripts *T* and *P* indicate isothermal and isobaric data, respectively.

model parameters for normal [14] and branched [15] hydrocarbon was performed, while cyclic hydrocarbons are under study [16]. The present work is part of a broader project; the development of a robust GCA-EoS model to predict VLE and LLE in biorefineries simulations.

2. Thermodynamic modeling

2.1. GCA-EoS development and applications

The first version of the GCA-EoS was developed for the modeling of phase equilibria found in the near critical fluid extraction and dehydration of oxygenated compounds from aqueous solutions [17,18]. GCA-EoS was obtained by the inclusion of a group contribution SAFT-like associating term to the GC-EoS model. Accounting the association term by a real group contribution approach was possible through the simplification of the radial distribution function to a value of one (see Appendix A for a detailed description of the

model). In this version, the definition of a unique hydroxyl group to represent the association effect of hydrogen bonding in water and alcohols, greatly simplifies the extension of the model to multicomponent mixtures. Moreover, in several cases the non-bonded fraction has analytical solution. This approach has been successfully applied to determine the parameters for a common hydroxyl group for water, primary and secondary alcohols.

Later on, Ferreira et al. [19,20] extended GCA-EoS to represent phase equilibria in mixtures containing acids, esters, and ketones, with water, alcohols, and any number of inert components. Self-association and solvation between the associating groups present in these mixtures were considered with specific expressions for each kind of association system, according to the number and type of associating groups (i.e. self- and/or cross-associating groups) present in the mixture. Table 1 reviews GCA-EoS applications in process design and optimization following both approaches.

A general routine was implemented following Michelsen and Hendriks [48] state function minimization approach to simplify the

Table 11
Comparison between GCA-EoS, ESD [109], CPA [110], NRHB [12] and sPC-SAFT [12] models accuracy for the binary systems alcohol + benzene.

Alcohol	T (K)	P (kPa)	$(\Delta P\%$ for isotherms and ΔT for isobars)/ Δy				
			NRHB	sPC-SAFT	CPA (1997)	ESD	GCA
Methanol	373, 413, 453, 493	312–5760	–	–	2.14/0.013	2.1/–	1.7/0.014
Ethanol	324–335	53	0.14/0.011	0.16/0.008	–	–	0.18/0.015
	298	12–16	–	–	1.23/0.008	–	1.10/0.015

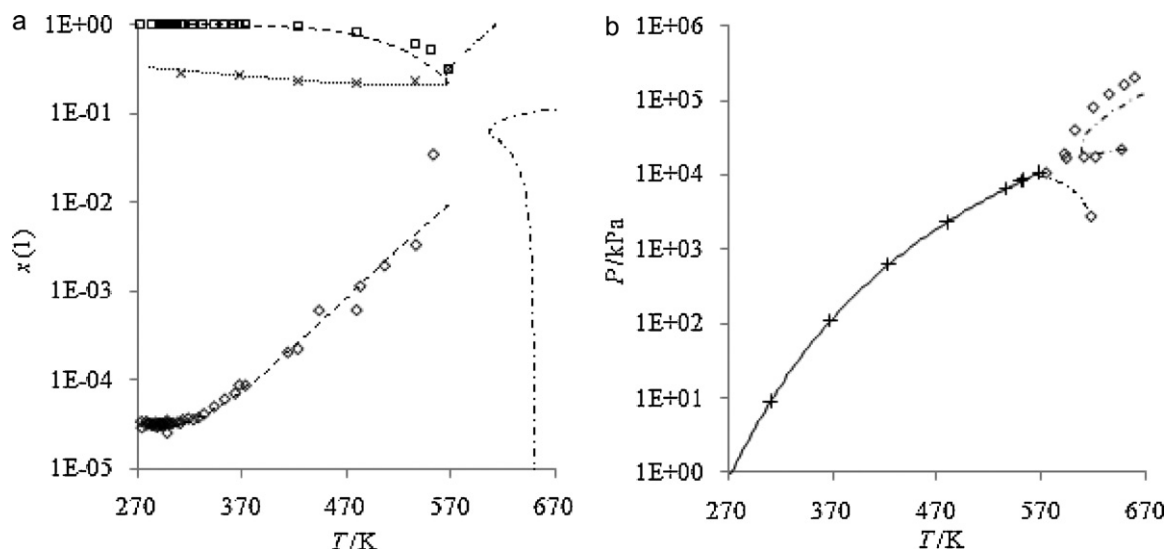


Fig. 3. Phase behavior of the system ethylbenzene(1)+water(2). (a): $x-T$ projection. Symbols: VLE experimental data [53,55], dashed lines: GCA-EoS LLE correlation, Solid line: GCA-EoS prediction of vapor phase composition, dotted-dashed lines: GCA-EoS prediction of critical locus. (b) $P-T$ projection. Symbols: experimental VLE vapor pressure curve (+) [55] and critical locus (\diamond) [60]. Lines: GCA-EoS prediction.

calculation of the association contributions to physical properties for the calculation of the fraction of non-associating sites and their first derivatives with respect to process variables. This generalized computational routine quantifies association and solvation effects by the interaction between any number of functional-associating groups with one or two associating sites [14,49]. This is enough to represent any compound with odd or even association sites. For instance water is represented as a 4C model using two equal groups with 2 sites (one electro-positive and one electro-negative). This implementation has already been applied to several systems containing multiple associating-solvating groups Table 2 summarizes applications of the upgraded GCA-EoS with the new procedure to solve fraction of non-bonded sites.

It is important to highlight the group contribution approach used in the association term of the model. The same OH group is used to build any alcohol molecule, therefore the number of fitted parameters is dramatically reduced, and of course this fact also

allows predicting phase behavior of systems for which no experimental data are available. Table 3 shows the self-associating and solvating groups available in GCA-EoS table of parameters. Moreover also different associating groups can be combined in a single compound. For instance, Sánchez et al. [10] predicted hydrocarbon solubility in aqueous alkanolamine solutions based on parameters fitted with binary data of, amines + alcohol [50], water + alcohol [14], and amines + water [10].

The upgraded GCA-EoS allows dealing with mixtures having several associating groups that can self-associate or solvate with others. Therefore, a re-parameterization of the model is being carried out, in this case special emphasis is given to achieve a predictive model for different types of equilibria (VLE, LLE or VLLE) together with accurate data correlation in a wide range of mixtures composition. The goal in this case is to develop a tool for making the entire phase behavior diagrams with a single set of parameters. Revised groups are indicated with asterisk in Table 3.

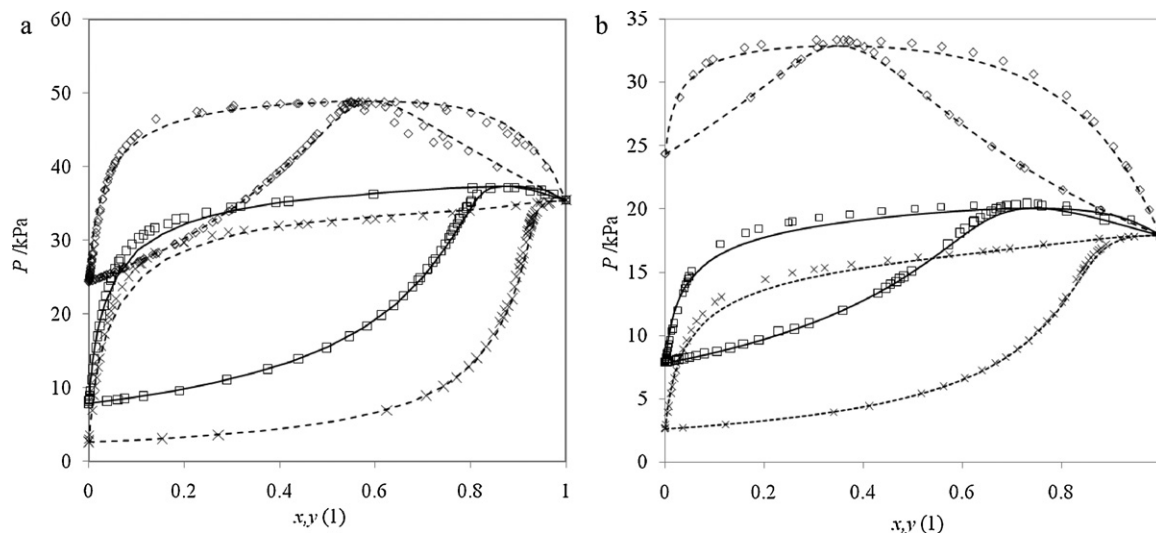


Fig. 4. (a) Vapor-liquid equilibria of the binary systems methanol(1)+(\diamond) benzene(2), (\square) toluene(2) and (\times) p -xylene(2) at 313.15 K [62,69]. Dashed lines: GCA-EoS correlation. Solid lines: predictions. (b) Vapor-liquid equilibria of the systems ethanol(1)+(\diamond) benzene(2), (\square) toluene(2) and (\times) p -xylene(2). Symbols: experimental data at 313.15 K [62]. Dashed lines: GCA-EoS correlation. Solid lines: predictions.

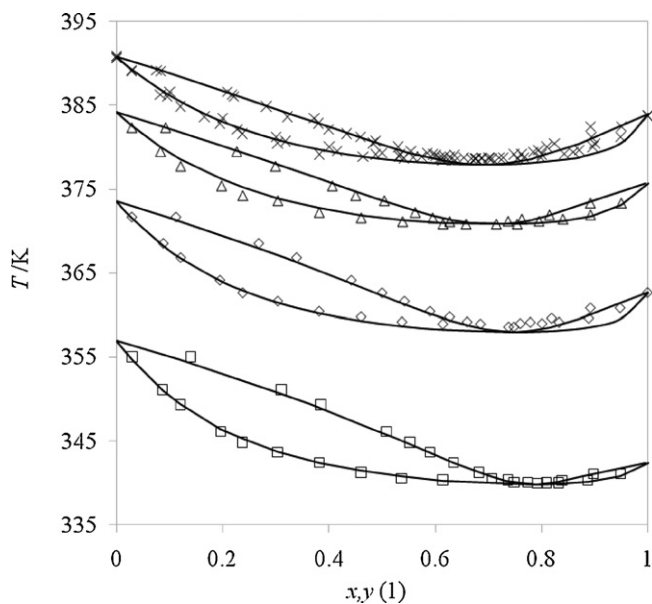


Fig. 5. Vapor-liquid equilibria of the binary system toluene(1)+1-butanol(2). Symbols: experimental data [67,105–107] at (□) 27 kPa, (◇) 53 kPa, (△) 80 kPa and (×) 100 kPa. Solid lines: GCA-EoS predictions.

2.2. Model extension to aromatic compounds

The extension of GCA-EoS table of parameters to aromatic compounds is based on parameterization done in previous works [14,15]. This means that only parameters for aromatic groups were fitted and no modification to previous parameters have been done in order to correlate experimental data. This section reports GCA-EoS parameters fitted in this work together with those required from previous works. Tables 4 and 5 report the pure-group energy and their corresponding binary energy interaction and non-randomness parameters, respectively. Table 6 shows parameters for the association contribution (volume and energy of association). All tables also report the type of experimental data used to fit each set of parameters and source of reference for those parameters determined in previous works. In previous GCA-EoS parameterization studies, binary interaction parameters

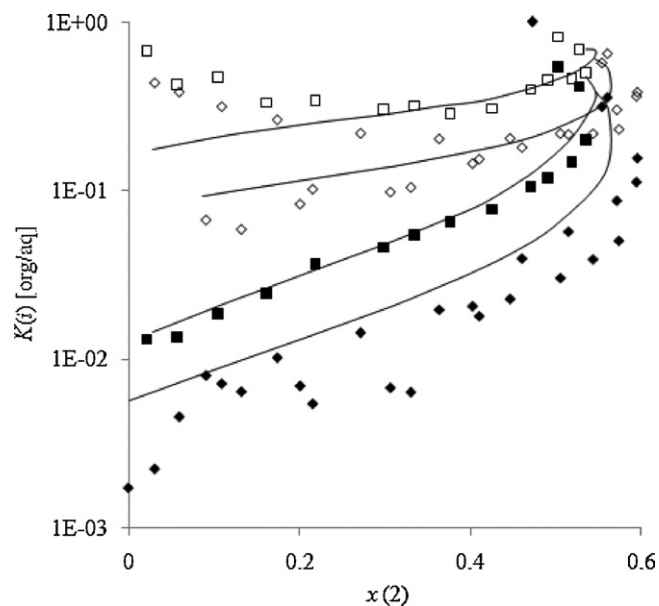


Fig. 7. Partition coefficient of methanol (empty symbols) and water (full symbols) of the ternary system water(1)+methanol(2)+benzene(3). Symbols: experimental data [111,121] at (◇) 303.15 K and (□) 333.15 K. Lines: GCA-EoS predictions.

of the alkane groups contained in water-insoluble compounds infinitely diluted in water, were found to have values different from the regular alkane groups [14,15,51]. This has a physical explanation; the environment of the alkane group in a paraffin+water binary is completely different than that, for instance, in an alcohol+water solution. Following this approach, the binary interaction parameters reported in Table 5 as $H_2O/ACCH_3^\infty$, $H_2O/ACCH_2^\infty$ and H_2O/ACH^∞ should be used in any application of the model that requires highly accurate predictions of the mutual solubility between water and aromatic hydrocarbons. Otherwise, regular aromatic alkane groups should be used. With these groups also a high mutual immiscibility for water+aromatic hydrocarbon is predicted together with the increase of partial miscibility due to the addition of a co-solvent (see Section 3 for ternary systems).

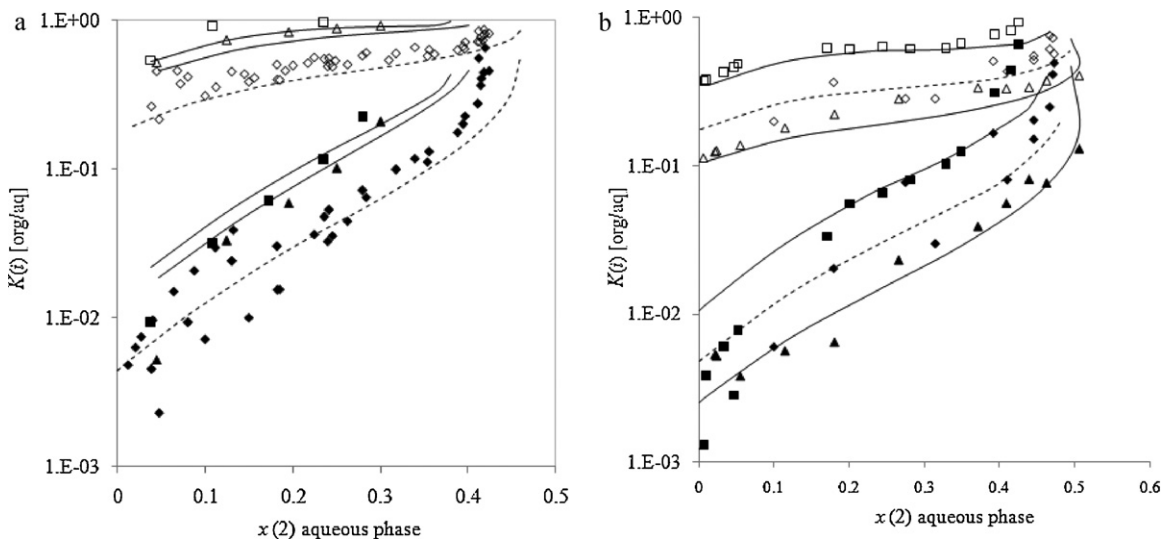


Fig. 6. (a) Partition coefficients (K_i) of the system water(1)+ethanol(2)+benzene(3) at (◇) 298, (△) 328 and (□) 337 K. Experimental data: [112–117]. Full symbols: K_1 ; empty symbols: K_2 . Dashed and solid lines: correlation and prediction, respectively. (b) Partition coefficients of the system water(1)+ethanol(2)+toluene(3) at (△) 278, (◇) 298 and (□) 323 K. Full symbols: K_1 ; empty symbols: K_2 . Experimental data [118–120]. Dashed and solid lines: GCA-EoS correlation and predictions, respectively.

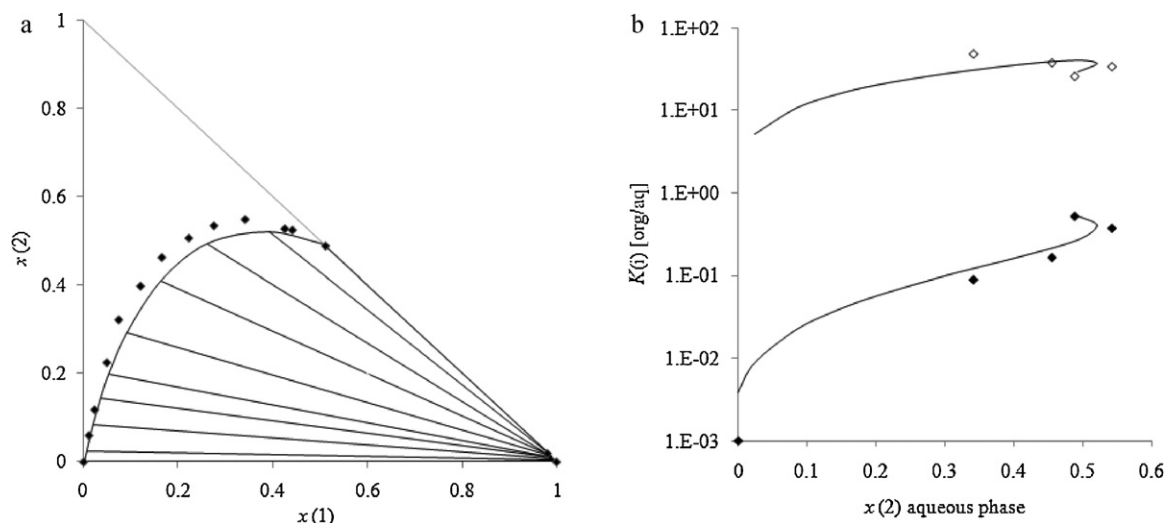


Fig. 8. (a) Liquid–liquid equilibria of the ternary system water(1)+butanol(2)+toluene(3). Symbols: experimental binodal curve [120] at 298.15 K. Solid lines: GCA-EoS prediction. (b) Water (◆) and butanol (◇) partition coefficients in the ternary system water(1)+butanol(2)+toluene(3). Dots: experimental data [120]. Solid lines: GCA-EoS prediction.

The critical diameters (d_c) for the repulsive contribution of the aromatic compounds are shown in Table 7 together with the model accuracy to predict their vapor pressure (percent average relative deviation). Experimental vapor pressure data for comparison was taken from DIPPR database [52].

3. Results and discussion

3.1. Water + BTEX and water + alkyl benzene

Table 8 summarizes the results obtained for each water+aromatic hydrocarbon binary system evaluated in this work (both correlations and predictions). This table reports the temperature and pressure range covered, the number of data-points (N), the deviations obtained with the GCA-EoS model, and the source of the experimental data. Figs. 1 and 2 show the GCA-EoS correlations (for benzene, *m*-xylene and ethylbenzene) and predictions of mutual solubility between water and BTEX and higher alkylbenzene, respectively. As it can be seen, GCA-EoS correlates and predicts with high accuracy the low solubility of BTEX in water, while in the hydrocarbon phase the model presents some deviations at high temperatures. A sensitivity analysis on the model parameters showed that this deviation is caused by the critical diameter of water. Since our objective is to get a single set of parameters for all the systems under study, we decided to keep for this parameter the value used in previous work (Figs. 1 and 2).

Fig. 3 shows the pressure–temperature phase behavior diagram of the binary system ethylbenzene+water, calculated with GPEC [61]. It is possible to see that GCA-EoS besides making a good correlation of the vapor–liquid–liquid equilibria is able to predict the location of the mixture critical points.

Table 9 shows a comparison between GCA-EoS and other four models that explicitly take into account association effects: ESD [4], CPA [6], NRHB [8] and sPC-SAFT [8]. In these works, different set of experimental data or temperature range were covered. For the sake of comparison, Table 10 gives GCA deviation in the same range of temperature and also in the complete range covered in this work. It is important to highlight that is difficult to make a fair comparison between a molecular model and a group contribution model. GCA-EoS is using the same set of parameters for predicting not only the systems shown in Table 10 but also those of Table 8. Moreover, in the case of toluene, the data set correlated with CPA

[6] was not included in GCA-EoS parameterization, nevertheless GCA-EoS prediction for the binary water + toluene is reported.

3.2. Alcohols + BTEX

Table 10 summarizes the results in correlation and prediction obtained for all the alcohol+aromatic hydrocarbon binary systems studied in this work. Similar to the previous table, it reports the temperature and pressure range covered, the number of data-points (N), the deviations obtained with the GCA-EoS model, and the source of the experimental data. Fig. 4 depicts GCA-EoS correlations and predictions of methanol (Fig. 4a) and ethanol (Fig. 4b) +BTEX vapor liquid equilibria. On the other hand, Fig. 5 shows GCA-EoS simulation of toluene + 1-butanol binary system. The model accurately predicts by group contribution the phase behavior and azeotropes location of this system.

The binary alkanol + benzene has also been correlated with ESD [109], CPA [110], NRHB [12], and sPC-SAFT [12]. Table 11 shows the comparison between GCA-EoS deviation and the reported deviation for those models. In this case, none of the shown datasets were included in GCA-EoS parameterization. GCA-EoS extrapolations are of similar accuracy than the other models. On the other hand, Grenner et al. [12] showed that NRHB and sPC-SAFT are able to predict without binary interaction parameters the system ethanol + benzene with good accuracy. The prediction of sPC-SAFT is better, with an average deviation of 0.46 K and 0.004 in vapor phase composition. GCA-EoS without binary interaction parameters predicts and average deviation of 0.41 K and 0.023 in vapor phase composition.

3.3. Ternary system BTEX + water + alcohol

The prediction of ternary data, based on parameters fitted only to binary data, gives accurate values of alcohol partition coefficients between hydrocarbon and aqueous phases. However, the binodal curve shows important deviations near the plait point region. Therefore, a few ternary datasets were included in the parameterization while others were left out to check the model predictive capacity, not only at different temperatures but for other compounds. The ternary data of water + ethanol + benzene and water + ethanol + toluene at 298 K, respectively, were correlated. Fig. 6a and b shows ethanol and water partition coefficients for both correlated isotherms together with values predicted at

other temperatures. Fig. 7 shows GCA-EoS prediction of the partition coefficients for the system methanol + water + benzene (303 and 333 K). Experimental data available for this system is very scattered; however, GCA-EoS is in good agreement with the data of Gramajo de Doz et al. [111]. Finally, Fig. 8 depicts GCA-EoS predictions of the binodal curve (Fig. 8a) and partition coefficients (Fig. 8b) for the system water + butanol + toluene (298 K).

4. Conclusions

The GCA-EoS has been applied to a number of complex systems of importance in the petrochemical and natural gas industry, in the field of natural products and for food processing as well. This model is the first EoS of the SAFT family to include a group contribution approach for the Wertheim model. In this work the extension to aromatic hydrocarbons, water and alkanols mixtures is presented, GCA-EoS successfully correlates and predicts the experimental data.

List of symbols

2B	two sites associating group, one electronegative and one electropositive
3B	three sites associating group, one electronegative and two electropositive
4C	four associating sites group, two electronegative and two electropositive
A^{fv}	Helmholtz energy term describing free volume part
A^{att}	Helmholtz energy term describing attractive part
A^{assoc}	Helmholtz energy term describing association part
d_i	diameter of the component i (cm mol ⁻¹)
d_{ci}	hard sphere diameter of the component i (cm mol ⁻¹)
g_{ij}	attraction energy parameter for interactions between groups i and j (atm cm ⁶ mol ⁻¹)
k_B	Boltzman constant
k_{ij}, k_{ji}	binary interaction parameters
M_i	number of associating sites assigned to group i
NC	number of components in the mixture
NGA	number of associating groups
n_i	number of moles of component i
n_j^*	number of moles of associating group j
q	surface-area segments per mole
q_j	number of surface segments assigned to group j
\tilde{q}	total number of surface segments
T	temperature (K)
T_{ci}	critical temperature of component i (K)
T_r	reduced temperature
R	ideal gas constant
V	volume (cm ³)
x_i	mole fraction in liquid phase of component i
$X^{(k,i)}$	fraction of not bonded site k of group i
y_i	mole fraction in vapor phase of component i
z	number of nearest neighbors to any segment

Greek letters

α_{ij}, α_{ji}	non randomness parameters
$\Delta^{(k,i,l,j)}$	association strength between site k of group i and site l of group j (cm ³ mol ⁻¹)
$\Delta Z\%$	average relative deviation $(100/N) \sum 1 - (Z_{calc}/Z_{exp}) $
ΔZ	average absolute deviation $(1/N) \sum Z_{exp} - Z_{calc} $
$\varepsilon^{(k,i,l,j)}$	association energy between site k of group i and site l of group j (J)
$\kappa^{(k,i,l,j)}$	association volume between site k of group i and site l of group j (cm ³ mol ⁻¹)

v_{ij}	number of groups j in molecule i
$v_{assoc}^{(i,m)}$	number of associating group i in molecule m
ρ	density (mol cm ⁻³)
ρ_j^*	molar density of the associating group j (mol cm ⁻³)
θ_j	surface fraction of group j

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Appendix A. GCA-EoS mathematical model

There are three contributions to the residual Helmholtz energy in the GCA-EoS model: free volume, attractive and associating. The free volume and attractive contributions are based on Carnahan–Starling and NRTL models, respectively, and keep the same form as the original GC-EoS Skjold–Jørgensen equation [51,122].

The Carnahan–Starling repulsive term [51] follows the expression developed by Mansoori and Leland [123] for mixtures of hard spheres. It is a function of the critical hard sphere diameter d_c , characteristic of the pure-compound molecular size and has no binary or higher-order parameters.

$$\frac{A^{fv}}{RT} = 3 \frac{\lambda_1 \lambda_2}{\lambda_3} (Y - 1) + \frac{\lambda_2^3}{\lambda_3^2} (Y^2 - Y - \ln Y) + n \ln Y \quad (1)$$

with

$$Y = \left(1 - \frac{\pi \lambda_3}{6V} \right)^{-1} \quad (2)$$

$$\lambda_k = \sum_{i=1}^{NC} n_i d_i^k \quad (3)$$

where n_i is the number of moles of component i , NC stands for the number of components, V represents the total volume, R stands for universal gas constant and T is temperature.

The following generalized expression is assumed for the hard sphere diameter temperature dependence:

$$d_i = 1.065655 d_{ci} \left[1 - 0.12 \exp \left(-\frac{2T_{ci}}{3T} \right) \right] \quad (4)$$

where d_c is the value of the hard sphere diameter at the critical temperature, T_c , for the pure component.

There are three different ways to calculate d_c of each component: (i) direct calculation with the values of critical temperature and pressure so that the model fulfills the critical point and its conditions (first and second derivatives of pressure with regard to volume equal to zero) [51], (ii) fit d_c to an experimental pure-component vapor pressure data point (T_{sat} , P_{sat}) [51], and (iii) computation with the correlation proposed by Bottini et al. [124] for high molecular weight compounds.

In the case of permanent gases and molecular compounds, the first procedure must be used. For ordinary solvents method (ii) is generally applied; the d_c values obtained by this way are usually within 5% of the d_c given by method (i), but this difference is significant since pure component vapor pressures are sensitive to d_c [51]. Even more sensitive to the d_c value are the predictions of liquid–liquid equilibria. In this case, better results are achieved when d_c is closer to the value calculated with the critical point conditions (method i).

The attractive contribution to the residual Helmholtz energy (A^{att}) accounts for dispersive forces between functional groups. It is a van der Waals type contribution combined with a

density-dependent, local-composition expression based on a group contribution version of the NRTL model [125]. Integrating van der Waals EoS, $A^{att}(T,V)$ is equal to $-a \cdot n \cdot \rho$ with a the energy parameter, n the number of moles and ρ the mol density. For a molecular component a is computed as follows:

$$a = \frac{z}{2} q^2 g(T) \quad (5)$$

where g is the characteristic attractive energy per segment and q is the surface segment area per mole as defined in the UNIFAC method. The interactions are assumed to take place through the surface and the coordination number z is set equal 10 as usual. In GCA-EoS the extension to mixtures is carried out using the two fluids model NRTL model, but using local surface fractions like in UNIQUAC rather than local mole fractions. Therefore, the A^{att} for the mixture becomes

$$\frac{A^{att}}{RT} = -\frac{(z/2)\tilde{q}^2 g_{mix}(T, V)}{RTV} \quad (6)$$

where \tilde{q} is the total number of surface segments and g_{mix} the mixture characteristic attractive energy per total segments and are calculated as follows:

$$g_{mix} = \sum_{j=1}^{NG} \theta_j \sum_{k=1}^{NG} \frac{\theta_k g_{kj} \tau_{kj}}{\sum_{l=1}^{NG} \theta_l \tau_{lj}} \quad (7)$$

and

$$\tilde{q} = \sum_{i=1}^{NC} \sum_{j=1}^{NG} n_i v_{ji} q_j \quad (8)$$

where v_{ji} is the number of groups of type j in molecule i ; q_j stands for the number of surface segments assigned to group j ; θ_k represents the surface fraction of group k ;

$$\theta_j = \frac{1}{\tilde{q}} \sum_{i=1}^{NC} n_i v_{ji} q_j \quad (9)$$

$$\tau_{ij} = \exp\left(\alpha_{ij} \frac{\tilde{q} \Delta g_{ij}}{RTV}\right) \quad (10)$$

$$\Delta g_{ij} = g_{ij} - g_{jj} \quad (11)$$

g_{ij} stands for the attractive energy between groups i and j ; and α_{ij} is the non-randomness parameter. The attractive energy between unlike groups is calculated from the corresponding interactions between like groups:

$$g_{ij} = k_{ij}^* \sqrt{g_{ii} g_{jj}} \quad (k_{ij} = k_{ji}) \quad (12)$$

with the following temperature dependence for the energy and interaction parameters:

$$g_{ii} = g_i^* \left[1 + g_i' \left(\frac{T}{T_i^*} - 1 \right) + g_i'' \ln \left(\frac{T}{T_i^*} \right) \right] \quad (13)$$

and

$$k_{ij} = k_{ij}^* \left[1 + k_{ij}' \ln \left(\frac{2T}{T_i^* + T_j^*} \right) \right] \quad (14)$$

where g_i^* is the attractive energy and k_{ij}^* the interaction parameter at the reference temperature T_i^* and $(T_i^* + T_j^*)/2$, respectively.

The associating term A^{assoc} follows Wertheim's first order perturbation theory through a group-contribution expression [18]:

$$\frac{A^{assoc}}{RT} = \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right) + \frac{M_i}{2} \right] \quad (15)$$

In this equation NGA represents the number of associating functional groups, n_i^* the total number of moles of associating group i , $X^{(k,i)}$ the fraction of group i non-bonded through site k and M_i the number of associating sites in group i . The total number of moles of associating group i is calculated from the number $v_{assoc}^{(i,m)}$ of associating groups i present in molecule m and the total amount of moles of specie m (n_m):

$$n_i^* = \sum_{m=1}^{NC} n_m v_{assoc}^{(i,m)} \quad (16)$$

The fraction of groups i non-bonded through site k is determined by the expression:

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \rho_j^* X^{(l,j)} \Delta^{(k,i,l,j)} \right]^{-1} \quad (17)$$

where the summation includes all NGA associating groups and M_j sites. $X^{(k,i)}$ depends on the molar density of the associating group ρ_j^* and on the association strength $\Delta^{(k,i,l,j)}$:

$$\rho_j^* = \frac{n_j^*}{V} \quad (18)$$

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)} \left[\exp\left(\frac{\varepsilon^{(k,i,l,j)}}{RT}\right) - 1 \right] \quad (19)$$

The association strength between site k of group i and site l of group j depends on the temperature T and on the association parameters κ and ε , which represent the volume and energy of association, respectively.

The thermodynamic properties required to calculate phase equilibria are obtained by differentiating the residual Helmholtz energy. The association contributions to the compressibility factor Z and to the fugacity coefficient ϕ_i of component i in the mixture are given by:

$$\begin{aligned} Z^{assoc} &= -\frac{V}{n} \frac{\partial}{\partial V} \left(\frac{A^{assoc}}{RT} \right)_{T,n} \\ &= -\frac{V}{n} \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\frac{1}{X^{(k,i)}} - \frac{1}{2} \right) \left(\frac{\partial X_{ki}}{\partial V} \right)_{T,n} \right] \end{aligned} \quad (20)$$

$$\ln \phi_j^{assoc} = \frac{\partial}{\partial n_j} \left(\frac{A^{assoc}}{RT} \right)$$

$$\begin{aligned} \ln \phi_j^{assoc} &= \sum_{i=1}^{NGA} \left[v_{assoc}^{(j,i)} \left[\sum_{k=1}^{M_i} \left(\ln X^{(k,i)} + \frac{X^{(k,i)}}{2} \right) + \frac{M_i}{2} \right] \right. \\ &\quad \left. + n_i^* \sum_{k=1}^{M_i} \left(\frac{1}{X^{(k,i)}} - \frac{1}{2} \right) \left(\frac{\partial X^{(k,i)}}{\partial V} \right)_{T,V,n_i \neq i} \right] \end{aligned} \quad (21)$$

The final expressions of these contributions depend on the number of associating groups NGA and on the number of associating sites M_i assigned to each group i . Calculation of association effects is based on the minimization approach proposed by Michelsen and Hendriks [48] and Tan et al. [126] procedure to calculate the fraction of non-associating sites. Detailed of this procedure has been reported by Soria et al. [16].

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