

Modelling of phase equilibria for associating mixtures using an equation of state

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Available online 18 September 2004

Abstract

In the present work, the group contribution with association equation of state (GCA-EoS) is extended to represent phase equilibria in mixtures containing acids, esters, and ketones, with water, alcohols, and any number of inert components. Association effects are represented by a group-contribution approach. Self- and cross-association between the associating groups present in these mixtures are considered. The GCA-EoS model is compared to the group-contribution method MHV2, which does not take into account explicitly association effects. The results obtained with the GCA-EoS model are, in general, more accurate when compared to the ones achieved by the MHV2 equation with less number of parameters. Model predictions are presented for binary self- and cross-associating mixtures.

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Keywords: Phase equilibria; Equation of state; Group-contribution model; Association

1. Introduction

The group contribution with association equation of state (GCA-EoS) was initially proposed by Gros *et al.* [1]. It results from the addition of a third contribution, which quantifies the association forces, to the original repulsive and attractive terms of the group-contribution equation of state, GC-EoS [2,3].

The GCA-EoS was successfully applied to multi-component mixtures containing water, alcohols, and any number of inert components by defining a single associating group, the hydroxyl group OH, to represent association effects in these mixtures [1]. This approximation resulted in very good representation of the thermodynamic properties and phase equilibria for solutions containing these associating components [1,4].

In this work, the GCA-EoS is extended to several cross-associating mixtures containing esters, ketones, alcohols, water, acids, aromatics, and alkanes. The parameterization strategy is described, followed by the presentation of correlation and prediction results obtained with the GCA-EoS. A comparison with the group-contribution equation of state based on the modified Huron–Vidal second order mixing rule (MHV2) [5,6] is made.

2. The group contribution with association equation of state

The total Helmholtz energy can be written as a sum of three terms

$$A = A^{\text{rep}} + A^{\text{attr}} + A^{\text{assoc}}. \quad (1)$$

The repulsive term is described by the Mansoori and Leland expression for hard-spheres [7] and the attractive

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contribution is a group-contribution version of a density dependent local composition expression (NRTL). The association term results from the application of the group-contribution approach based on the first order perturbation theory presented by Chapman *et al.* [8] and Huang and Radosz [9], of the Wertheim's statistical fluid association theory [10–13].

The expression for the association term of the residual Helmholtz energy is a function of the number of association groups NGA present in the mixture [1]

$$(A^R/RT)^{\text{assoc}} = \sum_{k=1}^{NGA} n_k^* \left\{ \sum_{A_k} (\ln X^{A_k} - X^{A_k}/2) + M_k/2 \right\}, \quad (2)$$

where X^{A_k} is the fraction of group k not associated at site A, M_k is the number of sites and n_k^* is the number of moles of the correspondent association group k . The remaining equations that describe the association term are given in appendix A.

Gros *et al.* [1] defined one associating group, the hydroxyl group OH, to represent association effects in mixtures containing water, alcohols, and any number of inert components. Each water or alcohol molecule was considered to have one associating group with two sites (one electronegative site O and one electropositive site H). The rigorous model for the alcohol group with two electronegative sites (A and B) and one electropositive site (C) is replaced by the approximate model with only one electronegative site and one electropositive site (A and B, respectively). The rigorous model for water (two electronegative sites + two electropositive sites) is also replaced by the hydroxyl associating group.

2.1. Model development for new associating groups

The introduction of new associating groups besides the hydroxyl group gives rise to the effect of cross-association that will be discussed later. In this work, the model is

extended to mixtures containing, additionally, three new associating groups:

- The carboxylic acid association group COOH with one site capable of both self- and cross-associating.
- The ester association group COOR with one site that does not self-associate but can cross-associate with groups that have one electropositive site.
- The ketone association group COR with one site that does not self-associate but can cross-associate with groups that have one electropositive site.

Therefore, the model is extended to mixtures containing four possible associating groups as described in table 1. The same nomenclature proposed by Huang and Radosz [9] is used to classify the different sites and associating groups.

The number of sites assigned to each associating group is represented schematically on the first column of table 1. The second column shows the different assumptions concerning the association strengths between each pair of sites. Finally, the third column presents the association parameters that have to be fitted.

As can be seen from table 1, the double hydrogen bond of the acids is represented by a strong single bond between sites A. The ester group is represented by a unique electron-donor site and, that is also the case for the ketone group that has its own electron-donor site. These two latter associating groups (ester and ketone) do not self-associate, *i.e.*, their self-association strengths are zero.

The groups defined in table 1 are able to cross-associate in some situations. Table 2 describes the cross-association models developed in this work. The cross-association parameters are usually estimated by establishing appropriate combining rules between the self-association parameters and/or by treating them as additional adjustable parameters using thermodynamic data for cross-associating mixtures.

TABLE 1
Self-association models defined in the GCA-EoS

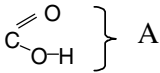

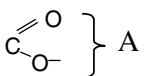

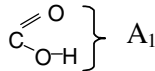

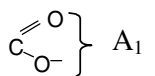

Self-association	Assumptions	Association parameters
Acid		$\Delta_{AA} \neq 0$ ϵ_{AA} κ_{AA}
Hydroxyl		$\Delta_{AB} \neq 0$
Ester		$\Delta_{AA} = \Delta_{BB} = 0$ $\Delta_{AA} = 0$ ϵ_{AB} κ_{AB}
Ketone		$\Delta_{AA} = 0$

TABLE 2
Cross-association models defined in the GCA-EoS model

Cross-association	Assumptions	Cross-association parameters
Acid-hydroxyl 	$\Delta_{A_1A_1} \neq 0, \Delta_{A_2B_2} \neq 0$	$\varepsilon_{A_1A_2} = \varepsilon_{A_1B_2} = (\varepsilon_{A_1A_1} + \varepsilon_{A_2B_2})/2$
Acid-ester 	$\Delta_{A_1A_2} = \Delta_{A_1B_2} \neq 0$ $\Delta_{A_1A_1} \neq 0, \Delta_{A_2A_2} = 0$	$\kappa_{A_1A_2} = \kappa_{A_1B_2} = (\kappa_{A_1A_1} \kappa_{A_2B_2})^{1/2}$ $\varepsilon_{A_1A_2} \quad \kappa_{A_1A_2}$
Ester-hydroxyl 	$\Delta_{A_1A_2} \neq 0$ $\Delta_{A_1A_1} = 0, \Delta_{A_2B_2} \neq 0$	$\varepsilon_{A_1B_2} \quad \kappa_{A_1B_2}$
Ketone-hydroxyl 	$\Delta_{A_1A_2} = 0, \Delta_{A_1B_2} \neq 0$ $\Delta_{A_1A_1} = 0, \Delta_{A_2B_2} \neq 0$ $\Delta_{A_1A_2} = 0, \Delta_{A_1B_2} \neq 0$	$\varepsilon_{A_1B_2} \quad \kappa_{A_1B_2}$

Suresh and Elliot [14] proposed the following geometric mean with respect to the association strength:

$$\Delta^{A_iB_j} = (\Delta^{A_i} \Delta^{B_j})^{1/2}. \quad (3)$$

Fu and Sandler [15] used the geometric mean of the energies of association of the pure components and the arithmetic mean of the association volumes:

$$\varepsilon^{A_iB_j} = (\varepsilon^{A_i} \varepsilon^{B_j})^{1/2}, \quad \kappa^{A_iB_j} = (\kappa^{A_i} + \kappa^{B_j})/2. \quad (4)$$

Other alternative combining rules were also proposed [16]:

$$\varepsilon^{A_iB_j} = (\varepsilon^{A_i} + \varepsilon^{B_j})/2, \quad \kappa^{A_iB_j} = (\kappa^{A_i} + \kappa^{B_j})/2, \quad (5)$$

$$\varepsilon^{A_iB_j} = (\varepsilon^{A_i} + \varepsilon^{B_j})/2, \quad \kappa^{A_iB_j} = (\kappa^{A_i} \kappa^{B_j})^{1/2}, \quad (6)$$

$$\varepsilon^{A_iB_j} = (\varepsilon^{A_i} \varepsilon^{B_j})^{1/2}, \quad \kappa^{A_iB_j} = (\kappa^{A_i} \kappa^{B_j})^{1/2}. \quad (7)$$

Several authors [16,17] have concluded that the optimal combining rules for the cross-association parameters are the arithmetic mean of the self-association energies and the geometric mean of the self-association volumes. Additionally, this rule has a theoretical background [16,17]. Therefore, in this work, the combining rules given by equation (6) were adopted.

For the cross-association between one associating group that can self-associate (hydroxyl or acid groups) and one group that can solely cross-associate (the ketone or ester groups), it is necessary to fit those cross-association parameters to experimental data, simultaneously with the attractive parameters.

After defining which groups are present in the mixture, the association contributions for the compressibility factor Z and the fugacity coefficient $\ln \hat{\phi}_i$ can be obtained from the Helmholtz energy of association. The original expressions [8] involve the calculation of derivatives of the fraction of non-bonded sites. More re-

cently, some researchers [18,19] have presented and discussed a simpler but equivalent mathematical expression that does not include any derivative of X^{A_k} . The general expressions that result from applying this much simpler mathematical approach to the group-contribution association expressions are presented in appendix A.

It is interesting to analyze the equations obtained for Z and $\ln \hat{\phi}_i$ for some particular cases.

Case I. One self-associating group with one site (acid group):

$$Z^{\text{assoc}} = -n_k^* \{ \rho \Delta (X^{\text{mon}})^2 \} / (2n), \quad (8)$$

$$\ln \hat{\phi}_i^{\text{assoc}} = v^{k,i} \ln X^{\text{mon}}. \quad (9)$$

Case II. One self-associating group with two sites (alcohol):

$$Z^{\text{assoc}} = -n_k^* \rho \Delta X^{\text{mon}} / n, \quad (10)$$

$$\ln \hat{\phi}_i^{\text{assoc}} = 2v^{k,i} \ln X^{\text{mon}}. \quad (11)$$

These expressions can be further simplified when applied to a binary mixture where one of the components is infinitely diluted in the other. At very low concentrations of the associating component, its monomer fraction will be close to one, *i.e.*, the component behaves as not associated at all. On the other hand, at higher concentrations, a high degree of association takes place. Therefore, for the calculation of self-association parameters, pure component thermodynamic properties of the associating component are a convenient source of experimental data.

When dealing with problems of cross-association it is possible to find an analytical solution for the fraction of non-associated groups in the cases where two associating groups are present. In this case, a cubic or quartic equation is obtained that can be solved analytically. Kraska [20] presents a review on several analytical solutions for these and other cross-association models.

3. Parameterization

Table 3 shows the temperature and pressure ranges for the (vapour + liquid) equilibria data used, together with the sources of the experimental information. The experimental database used in the optimization step includes vapour pressure (P^{vap}) of pure carboxylic acids [21]; binary low-pressure (vapour + liquid) equilibria (LPVLE) for (carboxylic acids + alkanes) [22,23], (carboxylic acids + alcohols) [22], (carboxylic acids + esters) [22,24], and (carboxylic acids + water) [22,25,26]; LPVLE for (benzene + alcohols) [22,27]; and high-pressure (vapour + liquid) equilibria for (water + ketones) [28–30]. The interactions between the ester group and the alcohol (or water) group were estimated using binary LPVLE for (esters + alcohols) and (esters + water) [22]. In the same way, the interactions between the alcohol and ketone groups were estimated using binary LPVLE for (ketones + alcohols) [22,31].

3.1. Association parameters

In order to model association using the GCA-EoS model, it is necessary to determine the number of associating groups, the number of active sites in each group and the values of the corresponding association strengths. Carboxylic acids present a high degree of non-ideality even at low pressures, which can be ascribed to the formation of oligomers in both liquid and vapour phases. Generally only the formation of dimers is considered, and it is possible to find in the literature [22] the values of the vapour phase dimerization

constants for a number of carboxylic acids. In this work, a new associating group (COOH) was defined as having one associating site that self-associates by double hydrogen bonding.

Following the procedure adopted by Gros *et al.* [1] for the hydroxyl (OH) group, the COOH association parameters were obtained by reproducing the fraction of non-bonded molecules predicted by the SAFT equation for linear acids from propanoic to decanoic at saturated liquid conditions [9]. The values obtained for the energy and volume of association are $\varepsilon/k^{\text{COOH}} = 6300$ K and $\kappa^{\text{COOH}} = 2 \cdot 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively. As expected, the COOH energy of association is much larger than that of the OH group ($\varepsilon/k^{\text{OH}} = 2700$ K), which is in accordance with the higher degree of association of carboxylic acids. Figure 1 shows the results obtained. Huang and Radosz [9] determined both association parameters from pure component properties (vapour pressure and liquid density data).

The cross-association parameters between the hydroxyl group and the acid group were calculated using the combination rules given by equation (6). In this way, the cross-association parameters were calculated using the already existent self-association parameters and no additional association parameters had to be estimated.

However, for the cross-association between the ester group and the OH, or COOH groups, no combination rule can be established since the ester group does not self-associate. Therefore, it was decided to set them as adjustable parameters. As the hydrogen bonding will be between one site O in the ester group and one site H in the OH, or COOH groups, as a first estimate, the

TABLE 3
Experimental VLE database used for correlation (NS: number of data sets)

Systems	T range/K	P range/kPa	NS	References
CH ₂ /CH ₃ (hexane, heptane; octane; cyclohexane) + COOH (acetic acid, propanoic acid, butanoic acid, valeric acid, hexanoic acid, octanoic acid)	313 to 443	1 to 100	15	[22,23]
CH ₃ OH + COOH (acetic acid, propanoic acid)	333 to 411	20 to 180	5	[22]
CH ₂ OH (ethanol, 1-propanol, 1-butanol; 1-pentanol) + COOH (acetic acid, propanoic acid)	353 to 416	100	7	[22]
CHOH (2-propanol, 2-butanol) + COOH (acetic acid, propanoic acid)	357 to 412	100	3	[22]
H ₂ O + COOH (acetic acid, propanoic acid, butanoic acid)	298 to 432	4.1 to 360	9	[22,25,26]
CH ₃ COO (ethyl acetate; propyl acetate; butyl acetate) + COOH (acetic acid, propanoic acid)	315 to 398	3 to 200	11	[22]
CH ₂ COO (ethyl propionate) + COOH (propanoic acid)	323	3 to 20	1	[22,24]
CH ₂ OH (1-propanol, 1-butanol) + CH ₂ COO (methyl propionate, methyl butyrate)	328 to 368	19 to 85	7	[22]
CH ₂ OH (ethanol, 1-propanol, 1-butanol) + CH ₃ COO (ethyl acetate, butyl acetate)	323 to 328	22 to 53	3	[22]
H ₂ O + CH ₃ COO (methyl acetate, ethyl acetate, propyl acetate; butyl acetate)	298 to 353	8.1 to 130	8	[22]
H ₂ O + CH ₃ CO (acetone and 2-butanone)	308 to 523	18 to 6800	9	[28–30]
CH ₂ OH (ethanol, 1-propanol) + CH ₃ CO (acetone, 2-butanone)	328 to 368	44 to 100	4	[22]
CHOH (2-propanol) + CH ₂ CO (3-pentanone)	355 to 373	100	1	[22,31]
CH ₂ OH (ethanol, 1-propanol, 1-butanol) + ACH (benzene)	313 to 403	15 to 193	12	[22,27]

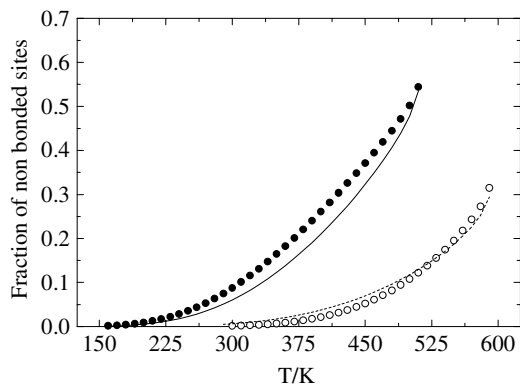


FIGURE 1. Fraction of non-bonded sites plotted against temperature. GCA-EoS: (●) ethanol; (○) acetic acid. SAFT-EoS: ethanol (—); acetic acid (---).

TABLE 4
GCA-EoS self and cross-association parameters

		Self-association	
		$(\epsilon_{ij}/k)/K$	$\kappa_{ij}/(\text{cm}^3 \cdot \text{mol}^{-1})$
COOH	6300.0	0.0200	
OH	2700.0	0.8621	
		Cross-association	
<i>i</i>	<i>j</i>	$(\epsilon_{ij}/k)/K$	$\kappa_{ij}/(\text{cm}^3 \cdot \text{mol}^{-1})$
COOH	OH	4500.0	0.1313
	COOR	3248.8	0.7786
OH	COOR	2105.3	0.9916
	RCOR	2485.0	0.5000

values of the self-association parameters values for the OH group were used. The ketone group has the same type of association, *i.e.*, it can cross-associate with the OH group but does not self-associate. The same procedure was followed for the case of the ester associating group. The corresponding self and cross-association parameters obtained in this work are presented in table 4.

3.2. Attractive parameters

The group-contribution attractive term includes five pure-group parameters (T^* , q , g^* , g' , and g'') and four binary interaction parameters (the symmetrical k_{ij}^* and k'_{ij} , and the asymmetrical non-randomness

TABLE 6
Binary interaction parameters in the attractive term

<i>i</i>	<i>j</i>	k_{ij}	Experimental information
COOH	CH ₃ /CH ₂	0.8520	LPVLE acids-alkanes
	CHOH	1.1295	LPVLE acids-alcohols
	CH ₂ OH	1.0383	LPVLE acids-alcohols
	CH ₃ OH	1.0256	LPVLE acids-methanol
	H ₂ O	1.0479	LPVLE acids-water
	CH ₃ COO/CH ₂ COO	1.0000	LPVLE acids-esters
CH ₂ OH	CH ₂ COO	1.0000	LPVLE alcohols-esters
	CH ₃ COO	1.0174	LPVLE alcohols-esters
	CH ₃ CO	0.9790	LPVLE alcohols-ketones
	ACH	0.9670	LPVLE alcohols-aromatics
H ₂ O	CH ₃ COO	1.0000	LPVLE water-esters
	CH ₃ CO	1.0000	HPVLE water-ketones

parameters α_{ij} and α_{ji}). The meaning of these parameters has been given previously [2,3].

The new acid group was added to the GCA-EoS parameter table. The attractive-energy parameters between this group and the paraffinic (CH₃ and CH₂), alcohol (CHOH, CH₂OH, CH₃OH), water (H₂O), and ester (CH₃COO and CH₂COO) functional groups were estimated using the experimental VLE database presented in table 3. It should be mentioned that neither temperature dependent parameters nor asymmetrical non-randomness parameters was estimated ($k'_{ij} = 0$ and $\alpha_{ij} = \alpha_{ji} = 0$).

Besides the association parameters, it was only necessary to calculate binary interaction parameters in some cases (*e.g.* CH₃COO/CH₂OH; CH₃CO/CH₂OH).

Tables 5 and 6 show the pure-group and the binary interaction parameters, respectively, together with the type of experimental data used in their estimation.

3.3. Repulsive parameters

The critical diameter of components where the group described in the attractive term coincides with the molecule (H₂O, CH₃OH) is given, rigorously, by the following expression [3]:

$$d_c = (8.943 \cdot 10^{-2} RT_c/P_c)^{1/3}. \quad (12)$$

For the remaining cases, the critical diameter is fitted to a point of the vapour pressure curve, usually the normal boiling point.

TABLE 5
Pure group parameters in the attractive term

Group	Ti*/K	q	g^{**}	g'	g''	Experimental information
COOH	600	1.224	999600.5	0.0	0.0	P^{vap} and LPVLE acids-alkanes

4. Results and discussion

In this section some of the GCA-EoS correlation and predictions are presented. For comparison, the results obtained with the group-contribution equation of state MHV2 [5,6] are also shown. This model was chosen as it also follows a group-contribution approach for which an extensive table of parameters is available.

4.1. Self-associating (acids + alkanes)

The correlation of carboxylic acid (acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, and heptanoic acid) vapour pressures gave an average relative deviation of 4% within a reduced temperature range between 0.55 and 0.90. Figure 2 presents some GCA-EoS correlation and predictions for several organic acids.

Table 7 compares experimental vapour compressibility factors (Z) at saturation [32] with the GCA-EoS predictions. The low values of Z reflect the strong association of carboxylic acids in the vapour phase, even at low pressures. It is interesting to notice that the GCA-EoS is able to follow the slight increase of Z with temperature, evidenced by the experimental data.

Figure 3 presents the saturation vapour and liquid compressibility factors for acetic acid. As can be seen, the GCA-EoS is able to correctly follow the shape of the curve: Z^{vap} presents a maximum and then decreases until it reaches the critical point value. However, the MHV2 model is not able to predict this behaviour.

The interaction parameters between the groups CH_3/CH_2 and COOH were calculated using not only the vapour pressures of pure carboxylic acids, but also low pressure binary VLE data of alkanes and acids. Table 8 shows the average absolute deviation in composition δy and the average relative deviation in pressure $\delta P/P$

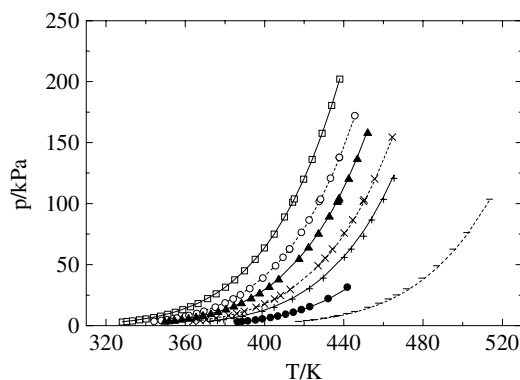


FIGURE 2. Vapour pressure of several organic acids plotted against temperature. Experimental data: (\blacktriangle) butanoic acid; (\times) 2-methylbutanoic acid; ($+$) pentanoic acid; ($-$) octanoic acid [34]; (\square) propanoic acid; (\circ) 2-methylpropanoic acid; (\blacklozenge) hexanoic acid [35]. GCA-EoS: (—) prediction; (---) correlation.

TABLE 7
 Z^{vap} prediction

Component	T/K	$Z_{\text{exp}}^{\text{vap}}$	$Z_{\text{calc}}^{\text{vap}}$	Error ^a (%)
Acetic acid	313	0.551	0.577	4.7
	323	0.569	0.583	2.5
	343	0.579	0.595	2.8
	363	0.595	0.606	1.8
Propanoic acid	323	0.611	0.646	5.7
	343	0.627	0.657	4.8
	363	0.638	0.668	4.7
	383	0.664	0.678	2.1
Butanoic acid	343	0.687	0.746	8.6
	363	0.706	0.752	6.5
	383	0.720	0.757	5.1
	403	0.741	0.761	2.7
Pentanoic acid	363	0.793	0.847	6.8
	383	0.805	0.845	5.0
	403	0.807	0.843	4.5
	423	0.801	0.840	4.9

$$^a \text{Error} = \{[Z_{\text{calc}} - Z_{\text{exp}}]/Z_{\text{exp}}\}.$$

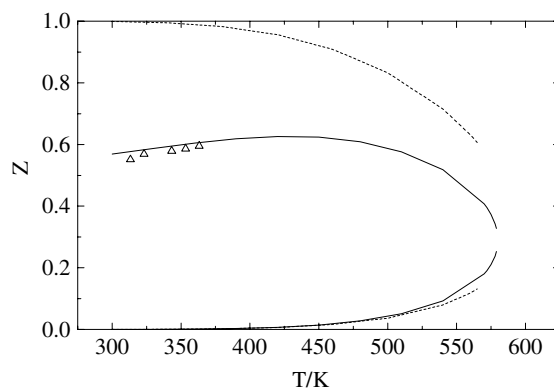


FIGURE 3. Saturation compressibility factor plotted against temperature for acetic acid: (\triangle) [32]; (—) GCA-EoS prediction; (---) MHV2 prediction.

for both models. The GCA-EoS significantly improves the results when compared with the MHV2 model. Satisfactory results are obtained as can be observed from figures 4 and 5. A more accurate description of the azeotropes is obtained by the GCA-EoS model compared to the MHV2 model.

The same parameters obtained by correlating low-pressure VLE of acids and alkanes were applied to higher pressures. Figure 6 shows the solubility predictions of ethane in nonanoic acid. Satisfactory results are obtained. As a first approximation, the interaction $\text{C}_2\text{H}_6\text{-COOH}$ was set equal to the interaction $\text{CH}_3\text{-COOH}$.

4.2. Self-associating (alcohols + aromatics)

The mixtures containing alcohols and aromatics only contain the OH associating group. The interaction

TABLE 8
Correlation results for VLE of acids and alkanes

System	NP ^a	T/K	P/kPa	GCA-EoS		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Heptane + propanoic acid	7	323	8.7 to 18	7.4	0.6	13.6	4.7
Octane + butanoic acid	13	398 to 434	100	3.5	2.7	10.0	2.8
Octane + acetic acid	17	378 to 397	100	3.6	2.2	10.4	4.8
Octane + acetic acid	18	343	19 to 29	2.6	1.6	2.4	10.3
Heptane + acetic acid	15	303	7.1 to 9.1	3.0	0.8	2.0	10.5
Heptane + valeric acid	5	323	11 to 17	1.6	0.30	5.7	0.51
	14	348	16 to 44	3.0	0.60	7.0	0.80
	11	373	23 to 91	6.1	1.8	6.4	0.96
Hexanoic acid + octanoic acid	11	373 to 395	1.3	5.1	1.5	5.1	1.4
	15	423 to 443	13	5.2	1.6	3.7	3.8
Cyclohexane + acetic acid	10	352 to 389	100	3.1	2.3	5.5	5.8
	9	313	8.6 to 25	6.1	3.7	16.0	4.1
Hexane + acetic acid	9	313	10 to 37	3.4	1.0	7.6	5.1
Hexane + propanoic acid	9	313	4.1 to 37	4.3	0.38	2.2	2.4
Cyclohexane + propanoic acid	9	313	3.2 to 24	3.9	0.85	9.3	1.6
Average deviations				4.0	1.5	6.7	4.5

^a NP, number of experimental points.

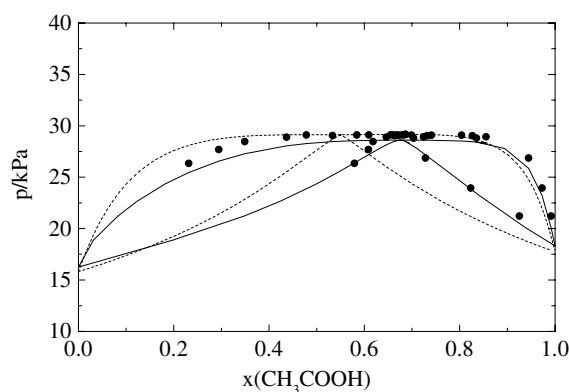


FIGURE 4. (Vapour + liquid) equilibrium of (acetic acid + octane) at 343 K: (●) [22]; (—) GCA-EoS correlation; (---) MHV2 prediction.

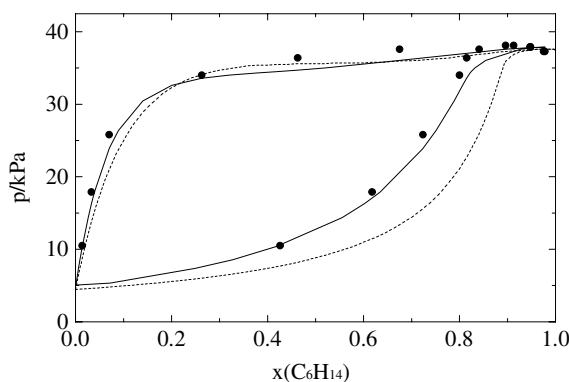


FIGURE 5. (Vapour + liquid) equilibrium of (hexane + acetic acid) at 313 K: (●) [23]; (—) GCA-EoS correlation; (---) MHV2 prediction.

between the attractive groups $\text{CH}_2\text{OH}/\text{ACH}$ was obtained by correlating the binary VLE data shown in table 9 using one interaction parameter k_{ij} . Table 9 shows

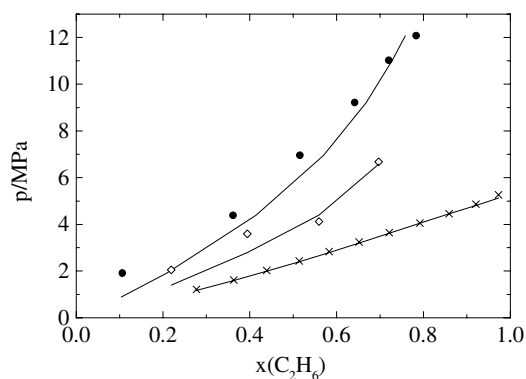


FIGURE 6. (Vapour + liquid) equilibrium of ethane and several solutes: (●) nonanoic acid at 353 K [36]; (◇) octanol at 318 K [37]; (×) octane at 313 K [38]; (—) GCA-EoS prediction.

the average relative deviations obtained using the GCA-EoS model and the MHV2 model. The MHV2 results in slightly lower average errors for these systems. However, it should be mentioned that the GCA-EoS only uses one symmetrical temperature independent $k_{\text{CH}_2\text{OH},\text{ACH}}$ parameter. Figure 7 presents some predictions using both models.

4.3. Cross-associating mixtures with OH and COOH groups

As mentioned before, the cross-association parameters between the OH associating group and the COOH group were obtained using the geometric rule for the volume of association and the arithmetic rule for the energy of association. For these systems, good predictions were obtained without further estimating interaction parameters.

TABLE 9
Correlation results for VLE of aromatics and alcohols

System	NP ^a	T/K	P/kPa	GCA-EoS		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Benzene + ethanol	12	318	36 to 41	2.2	1.2	1.7	0.88
	11	313	19 to 34	2.9	0.9	1.2	0.92
	13	341 to 350	100	1.9	1.7	1.8	1.04
	11	333	50 to 76	0.8	2.0	1.5	0.97
Benzene + 1-propanol	11	318	16 to 32	3.2	0.4	0.59	0.37
	12	349 to 365	100	2.9	1.9	2.0	2.1
	10	328	17 to 34	1.6	0.9	0.77	0.82
	13	348	51 to 95	1.0	1.1	1.2	0.85
Benzene+1-butanol	10	376 to 403	193	4.3	1.6	1.8	1.2
	7	313	21 to 24	4.3	0.1	1.2	0.074
	9	318	15 to 30	3.0	0.4	0.89	0.14
	18	353 to 390	100	2.5	0.9	0.85	0.40
Average deviations				2.5	1.1	1.3	0.83

^a NP, number of experimental points.

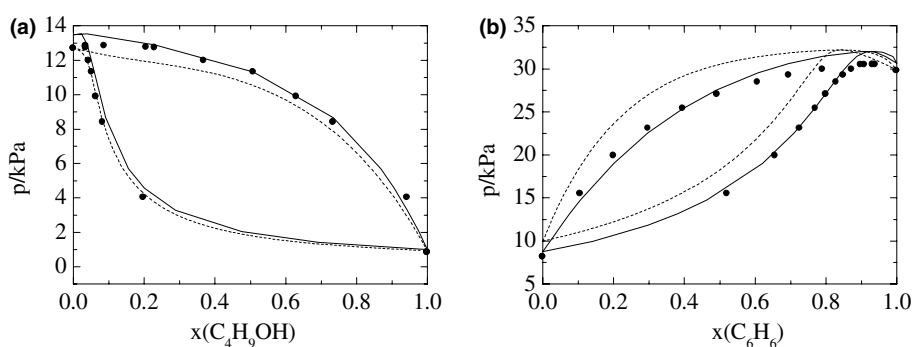


FIGURE 7. (Vapour + liquid) equilibrium predictions: (a) (1-butanol + benzene) at 298 K [39]; (b) (benzene + 2-butanol) at 318 K [40]. Model predictions: (—) GCA-EoS; (---) MHV2 prediction.

To improve the description of VLE for these systems a k_{ij} interaction parameter was estimated between the acid group and each of the alcohol attractive groups (CH_3OH , CH_2OH , and CHOH). Table 10 shows the average relative deviations obtained using the GCA-EoS model (both correlation and prediction results) and with the MHV2 model for cross-associating (alcohols and acids).

The water/acid interaction was obtained by correlating binary VLE data shown in table 11 using one interaction parameter k_{ij} . The MHV2 results in slightly lower average errors for these systems. Figure 8 gives the predictions for the (water + acetic acid) system at several pressures.

4.4. Cross-associating mixtures with COOH and COOR groups

As mentioned before, two cross-associating parameters must be estimated, as the ester group does not

self-associate. The cross-association parameters were calculated using low pressure VLE data for acids and esters. As a first estimate, for the optimization step, it was assumed that the association parameters between the COOR and COOH groups were equal to the ones of the alcohol group ($\epsilon_{\text{OH}}/k = 2700 \text{ K}$ and $\kappa_{\text{OH}} = 0.8621 \text{ cm}^3 \cdot \text{mol}^{-1}$). Furthermore, it was considered that $k_{\text{CH}_3\text{COO,COOH}} = 1.0$ and $\alpha_{\text{CH}_3\text{COO,COOH}} = \alpha_{\text{COOH,CH}_3\text{COO}} = 0.0$. The final values obtained for the cross-association parameters are: $\epsilon_{\text{COOH,COOR}}/k = 3249 \text{ K}$ and $\kappa_{\text{COOH,COOR}} = 0.7786 \text{ cm}^3 \cdot \text{mol}^{-1}$. Table 12 compares the correlation results from the GCA-EoS and the MHV2-EoS for mixtures containing esters and acids. Better results are obtained with the GCA-EoS.

4.5. Cross-associating mixtures with OH and COOR groups

For the cross-association between the hydroxyl and the ester associating groups, satisfactory results were ob-

TABLE 10
Results for VLE of alcohols and acids

Systems	NP	T/K	P/kPa	GCA-EoS prediction		GCA-EoS correlation		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Methanol + acetic acid	19	338 to 388	100	14.4	1.7	9.6	1.9	17.6	4.2
	6	333	20 to 93	4.0	2.5	5.7	1.8	6.3	3.7
	5	353	51 to 120	7.3	5.9	5.1	5.9	6.9	1.5
	6	363	63 to 180	8.6	2.9	5.5	2.4	9.2	5.2
Methanol + propanoic acid	21	338 to 411	100	10.2	2.9	7.9	3.5	16.8	2.3
Ethanol + propanoic acid	18	354 to 400	100	13.3	0.9	8.4	1.1	18.4	4.5
1-Propanol + propanoic acid	18	373 to 411	100	7.5	1.0	4.6	1.1	13.6	4.2
1-Butanol + propanoic acid	16	392 to 413	100	3.1	1.4	2.3	1.6	10.6	3.5
1-Pentanol + propanoic acid	19	411 to 416	100	2.1	2.2	3.1	2.4	9.8	4.7
Ethanol + acetic acid	16	353 to 388	100	13.1	1.4	7.7	1.2	16.2	5.5
1-Propanol + acetic acid	19	371 to 390	100	8.7	1.4	6.4	1.6	13.1	3.6
1-Butanol + acetic acid	19	392 to 396	100	2.9	2.2	4.0	2.5	9.3	3.6
2-Propanol + propanoic acid	18	358 to 412	100	15.0	0.9	6.1	1.2	17.6	4.5
2-Propanol + acetic acid	17	357 to 390	100	16.7	2.3	8.0	1.4	16.3	5.4
2-Butanol + acetic acid	18	375 to 391	100	10.5	2.2	4.8	1.9	12.9	4.5
Average deviations				9.5	1.9	6.1	1.9	14	4.1

TABLE 11
Results for VLE of water and acids

Systems	NP	T/K	P/kPa	GCA-EoS prediction		GCA-EoS correlation		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Water + acetic acid	11	298	2.4 to 3.1	9.4	6.9	5.2	2.2	13.5	6.6
	13	412	210 to 350	7.6	3.1	1.0	1.5	4.9	3.1
	13	372	62 to 100	8.6	4.4	2.5	1.5	8.5	4.8
Water + propanoic acid	8	313	4.1 to 7.1	9.6	4.4	4.4	3.2	3.9	2.0
	15	373	25 to 100	10.8	3.6	2.8	2.3	3.7	3.2
	18	353	19 to 46	10.3	3.3	6.5	4.0	2.7	3.3
Water + butanoic acid	26	373 to 432	100	12.0	4.7	5.5	4.1	4.2	0.81
	26	366 to 424	80	14.3	4.3	6.7	3.8	3.9	0.82
	25	356 to 405	54	14.7	4.2	7.0	3.7	4.2	1.0
Average deviations				11	4.3	5.1	3.2	5.0	2.4

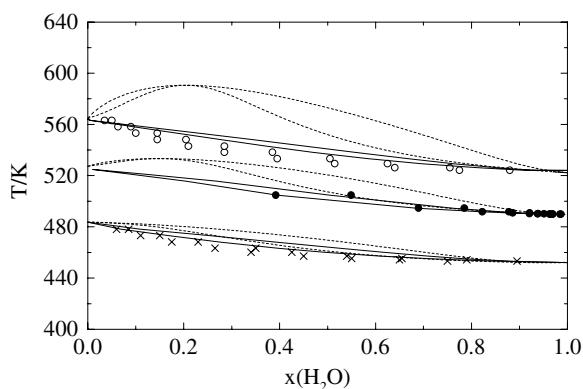


FIGURE 8. (Vapour + liquid) equilibrium of (water + acetic acid): (●) $P = 2.2$ MPa [25]; (○) $P = 3.9$ MPa [26]; (×) $P = 0.98$ MPa [26]; (—) GCA-EoS prediction; (---) MHV2 prediction.

tained. In fact, for the binary mixtures containing the CH_2OH and CH_2COO groups, no additional attractive parameters had to be estimated. For the interaction $\text{CH}_2\text{OH}/\text{CH}_3\text{COO}$, it was necessary to estimate a $k_{\text{CH}_3\text{COO},\text{CH}_2\text{OH}}$ (very close to one). Table 13 compares the results obtained for mixtures containing esters and alcohols. The MHV2 gives slightly better results than the GCA-EoS. Again, it should be mentioned that the GCA-EoS uses a smaller number of parameters to quantify the interaction between two associating groups.

As an alternative model, it was considered that no hydrogen bonding between esters and alcohols existed. That is, the (alcohol + ester) mixtures were considered to have only the OH self-associating group. It was verified that, to have the same level of accuracy as the

TABLE 12
Correlation results for VLE of esters and acids

Systems	NP	T/K	P/kPa	GCA-EoS		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Methyl acetate + acetic acid	14	333 to 378	100	3.7	3.3	3.9	8.4
	5	315 to 364	53	1.8	0.9	3.4	4.4
Ethyl acetate + acetic acid	11	323	8.1 to 37	3.6	4.0	5.5	1.9
	11	338	19 to 55	2.9	2.8	2.9	5.2
	11	346	27 to 73	3.1	3.6	3.0	4.4
	11	373	58 to 200	2.8	3.6	4.1	1.4
	6	353 to 381	100	2.6	2.8	4.9	4.1
	9	333 to 386	53	2.9	3.3	5.0	1.3
Propyl acetate + acetic acid	29	375 to 391	100	1.4	0.8	6.3	4.9
Butyl acetate + acetic acid	15	390 to 398	100	1.3	1.3	10	20
Ethyl acetate + propanoic acid	9	323.2	3 to 39	4.9	0.8	2.2	3.1
Ethyl propionate + propanoic acid	9	323.2	2.7 to 17	3.2	0.9	4.0	3.4
Average deviations				2.7	2.2	5.0	5.9

TABLE 13
Correlation results for VLE of alcohols and esters

Systems	NP	T/K	P/kPa	GCA-EoS		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
1-Propanol + methylpropanoate	18	328	18 to 42	3.2	2.6	1.29	0.91
	16	348	44 to 86	2.2	1.7	0.72	0.43
1-Propanol + methylbutanoate	17	333	21 to 26	1.9	1.8	2.34	0.99
	17	353	51 to 60	1.5	1.3	1.35	0.43
1-Butanol + methylpropanoate	20	348	22 to 83	2.4	1.3	0.7	1.4
1-Butanol + methylbutanoate	17	348	19 to 40	2.9	1.3	2.6	1.7
	17	368	46 to 79	2.6	1.0	0.9	0.7
Ethanol + ethyl acetate	11	328	44 to 54	2.5	1.7	2.1	0.6
1-Propanol + ethyl acetate	12	328	23 to 46	5.9	1.5	3.4	0.5
1-Butanol + butyl acetate	7	323 to 328	22	0.96	1.5	0.7	0.6
Average deviations				2.6	1.6	1.6	0.8

cross-associating model, it was necessary to use temperature dependent parameters between the attractive CH_2OH and CH_2COO groups, and asymmetric non random parameters. For the water/ester groups no additional parameters were estimated. Figures 9 and 10 are two examples of the GCA-EoS predictions for these systems.

4.6. Cross-associating mixtures with OH and RCOR groups

The cross-association parameters between the hydroxyl associating group (representing water and alcohols) and the ketone associating group were calculated using binary VLE for systems containing either water and ketones, or alcohols and ketones. Again, as a first estimate for the cross-association parameters, the values for the energy and volume of association for the hydroxyl group were used. An attractive interaction parameter between groups CH_3CO and CH_2OH was

estimated, using binary VLE data of primary alcohols and ketones (acetone and 2-butanone). Again, the k_{12} is close to one (0.979).

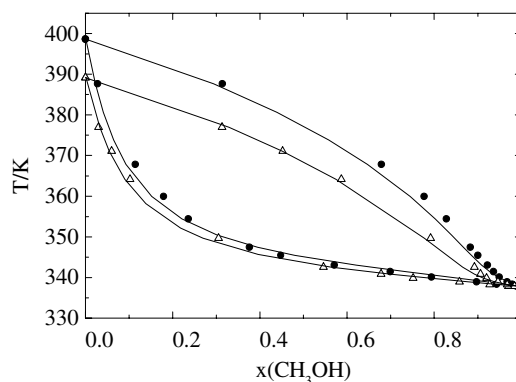


FIGURE 9. (Vapour + liquid) equilibrium at 101.325 kPa: (Δ) (methanol + isobutyl acetate); (\bullet) (methanol + butyl acetate) [41]; (—) GCA-EoS; (---) MHV2.

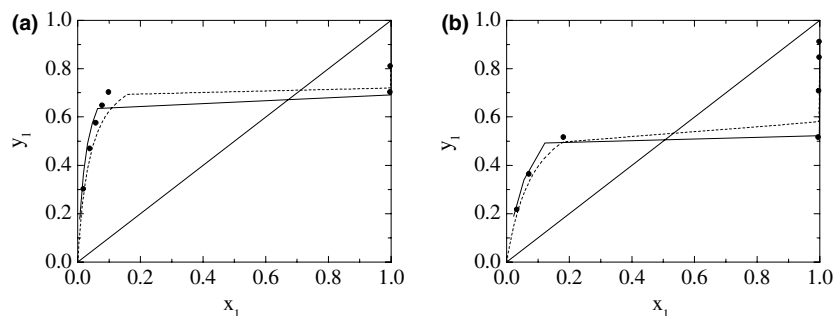


FIGURE 10. Vapour phase mole fraction versus liquid phase mole fraction: (a) butyl acetate (1) + water (2) at 317 K; (b) {water (1) + propyl acetate (2)} at 353 K. Experimental data [22]; (—) GCA-EoS prediction; (---) MHV2 prediction.

TABLE 14
Correlation results for VLE of ketones and water, or alcohols

Systems	NP	T/K	P/kPa	GCA-EoS		MHV2	
				$\delta P/P$ (%)	δy (%)	$\delta P/P$ (%)	δy (%)
Water + acetone	19	308	18 to 46	1.0	0.71	1.5	0.86
	22	373	110 to 370	3.1	0.8	4.7	2.0
	14	423	670 to 1200	3.5	1.9	3.1	1.8
	25	473	1600 to 2800	2.9	1.3	2.7	1.4
	14	523	4000 to 6800	1.3	0.6	0.8	0.90
Water + 2-butanone	25	347 to 373	100	1.8	1.5	2.9	2.6
	19	385 to 406	340	5.0	3.5	3.6	2.5
	18	412 to 435	690	4.7	3.2	3.4	2.5
	18	453 to 474	1700	3.9	1.8	3.0	1.2
Ethanol + acetone	4	331 to 342	100	1.7	2.5	1.3	1.8
Ethanol + 2-butanone	5	328	44 to 50	3.2	1.6	1.7	1.3
	5	348 to 350	100	1.1	1.6	2.1	1.3
1-Propanol + 2-butanone	15	353 to 368	100	1.7	0.8	1.3	0.7
3-Pentanone + 2-propanol	23	355 to 373	100	1.4	1.5	2.3	1.1
Average deviations				2.7	1.6	2.7	1.6

Table 14 presents the correlation results. Similar results are obtained using both models. For the (water + acetone) system, there are binary VLE data

of water and acetone over a wide range of temperature (between the temperatures 303 K and 523 K). The results can be seen in figure 11. Figures 12 and 13 show

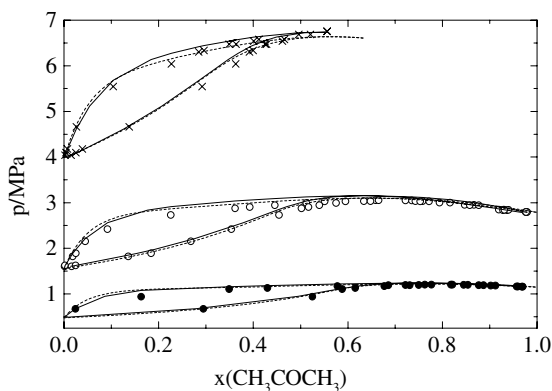


FIGURE 11. (Vapour + liquid) equilibrium of (water + acetone). Experimental data [28]: (●) 423 K; (○) 473 K; (×) 523 K. Models: (—) GCA-EoS correlation; (---) MHV2 prediction.

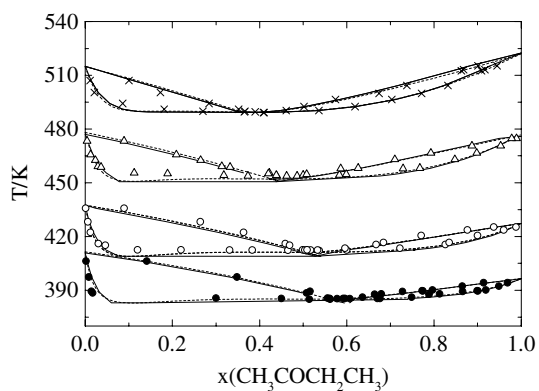


FIGURE 12. (Vapour + liquid) equilibrium of (2-butanone + water). Experimental data [30]: (×) 3.4 MPa; (△) 1.7 MPa; (○) 0.69 MPa; (●) 0.34 MPa. Models: (—) GCA-EoS; (---) MHV2 prediction.

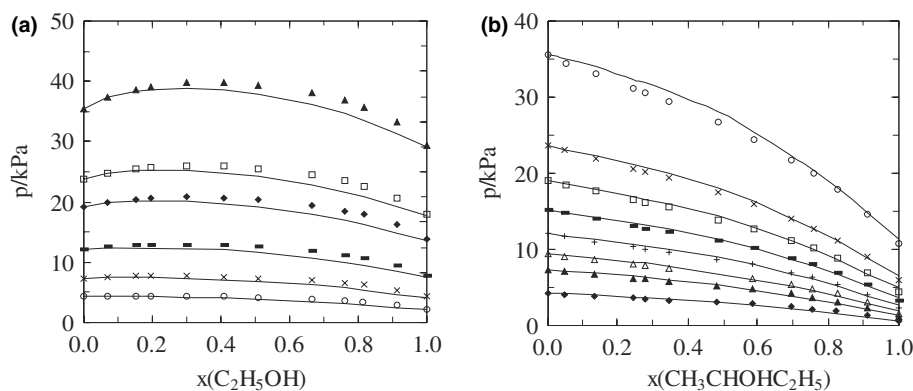


FIGURE 13. Vapour pressures of (butanone + alcohol). (a) (butanone + ethanol) [42]: (○) 278 K, (×) 288 K, (—) 298 K, (◆) 308 K, (□) 313 K, (▲) 323 K. (b) (butanone + 2-butanol) [43]: (◆) 278 K, (▲) 288 K, (△) 293 K, (+) 298 K, (—) 303 K, (□) 308 K, (×) 313 K, (○) 323 K. Model: (—) GCA-EoS prediction.

some of the GCA-EoS predictions for systems containing 2-butanone and water or one alcohol.

5. Conclusions

Association effects were represented by a group-contribution approach. The GCA-EoS was extended to mixtures containing acids, esters, aromatics, and ketones, with water, alcohols, and any number of inert components.

Cross-association parameters between the acid associating group and the hydroxyl associating group were calculated using the geometric mean for the volume of association and the arithmetic mean for the energy of association as combination rules.

A good representation of pure component properties and phase equilibria for mixtures of carboxylic acids with inert compounds, alcohols, and water at both low and high pressures is obtained.

Cross-association parameters between the ester associating group and either the acid, or the hydroxyl associating groups, were estimated using binary low-pressure (vapour + liquid) equilibria data. Again, very satisfactory results were obtained for these cross-associating mixtures.

The GCA-EoS model was compared to the group-contribution MHV2 method, which does not explicitly take into account association effects. The differences are in many cases very small. In this work, our intention is to compare two different approaches to model association effects: to use temperature dependent parameters which is the case of the MHV2 model and to modify a pure-component equation of state by adding an association term. In the case of acids, where association effects are very important, the GCA-EoS significantly improves the description of their phase equilibria. For the remaining cases, similar results are obtained. However, it should be mentioned that the GCA-EoS uses fewer

parameters to quantify the interaction between two associating groups. Another important conclusion from this work is the possibility of modelling association effects using a group-contribution approach.

The group-contribution nature of the GCA-EoS allows its application to highly associated mixtures, for which experimental information is scarce or not available over a wide density range.

Acknowledgements

O. Ferreira acknowledges financial support from the PRAXIS program, FCT, Lisbon Portugal (SFRH/BD/879/2000). E.A. Brignole acknowledges financial support from CONICET, Argentina and the Universidad Nacional del Sur.

Appendix A. The expression for the association term of the residual Helmholtz energy is a function of the fraction of group k not associated at site A, X^{A_k} [1]

$$X^{A_k} = \left(1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \rho_j X^{B_j} \Delta^{A_k B_j} \right)^{-1}, \quad (\text{A.1})$$

where ρ_j is the mole density of group j :

$$\rho_j = n_j^*/V. \quad (\text{A.2})$$

The number of moles of the association group k is calculated as follows:

$$n_k^* = \sum_{m=1}^{NC} v^{k,m} n_m, \quad (\text{A.3})$$

where $v^{k,m}$ is the number of groups k in molecule m and n_m is the number of moles of component m .

The association strength ($\Delta^{A_k B_j}$) is a simplified expression of the one proposed by Huang and Radosz

[33], since it does not include the radial distribution function g' . In this way, the group-contribution character of the model is preserved [1]

$$\Delta^{A_k B_j} = \kappa^{A_k B_j} \left\{ \exp(\varepsilon^{A_k B_j} / kT) - 1 \right\}. \quad (\text{A.4})$$

The association parameters between site A of group k and site B of group j are the association energy ε and the corresponding bonding volume κ . The general expressions to the association contributions for the compressibility factor Z and the fugacity coefficient $\ln \hat{\phi}_i$ can be obtained from the Helmholtz energy of association [1,18,19]:

$$Z^{\text{assoc}} = -\frac{1}{2} \sum_{k=1}^{NGA} \sum_{X^{A_k}} \frac{n_k^*}{n} (1 - X^{A_k}), \quad (\text{A.5})$$

$$\ln \hat{\phi}_i^{\text{assoc}} = \sum_{k=1}^{NGA} v^{k,i} \left\{ \sum_{X^{A_k}} (\ln X^{A_k}) \right\}. \quad (\text{A.6})$$

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