APPLICATION OF THE GCA-EOS MODEL TO THE SUPERCRITICAL PROCESSING OF ASSOCIATING OIL DERIVATIVES: FATTY ACIDS, ALCOHOLS AND TRIGLYCERIDES

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Supercritical processes are of interest in the fatty oil industry for a variety of applications: extraction and refining, removal of pollutants, recovery of specialties, hydrogenation of oils and derivatives, etc.
Typical process mixtures include heavy compounds and gases at near-critical conditions. At high pressures these asymmetric systems present a complex multi-phase behavior, difficult to model. This complexity increases if some of the mixture components are able to self- and/or cross associate.
In the present work, the group contribution with association equation of state (GCA-EOS) [3] is extended to represent high pressure phase equilibria in mixtures of supercritical gases (carbon dioxide, propane, ethane) with fatty oil derivatives, such as mono- and di-glycerides, fatty acids, alcohols, water and esters. Self- and cross-association between the associating groups present in these mixtures are considered.
Satisfactory correlation and prediction of equilibrium data are obtained. The capacity of the model to follow the behavior of the solutions towards the limit at infinite dilution of the associating components is of particular importance.

INTRODUCTION

Association and solvation effects have a major role in the properties of pure compounds and mixtures that can form hydrogen bonds. The group contribution with association equation of state GCA-EOS [3] explicitly takes into account those strong and highly directed attractive forces in its group contribution association term, which is based on Wertheim's theory as applied in the SAFT equation [4]. A single hydroxyl (OH) associating group was used to represent association effects in alcohols, water and any number of inert components [3]. In this work the GCA-EOS model is extended to mixtures containing additionally carboxylic acids and esters by defining two new associating groups: the COOH and COOR groups.

THE GCA-MODEL

The GCA-EOS results from the addition of a third term, which quantifies the association forces, to the original repulsive and attractive terms of the group contribution equation of state, GC-EOS [2]. The expression for the association term of the residual energy of Helmholtz is a function of the number of association groups *NGA* present in the mixture:

$$(A^R/RT)_{asoc} = \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i}\left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2}\right) + \frac{1}{2}M_i\right] \tag{1}$$

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

$$n_i^* = \sum_{m=1}^{NC} \gamma_{asoc}^{(i,m)} n_m \tag{2}$$

where $\gamma_{asoc}^{(i,m)}$ is the number of groups i in molecule m and n_m is the number de moles of molecule m. The mole fraction of group k, not associated trough site i, $X^{k,i}$ is given by:

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA}\sum_{l=1}^{M_j} \rho_j^* X^{(l,j)} \Delta^{(k,i,l,j)}\right]^{-1} \tag{3}$$

where ρ_j^* is the mole density of group j.

$$\rho_j^* = \frac{n_j^*}{V} \tag{4}$$

The association strength $\Delta^{k,i,l,j}$ between site k of group i and site l of group j is a function of the association energy ε and the corresponding bonding volume κ as follows:

$$\Delta^{(k,i,l,j)} = k^{(k,i,l,j)}\left[\exp\left(\frac{\varepsilon^{(k,i,l,j)}}{kT}\right) - 1\right] \tag{5}$$

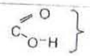
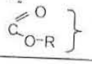
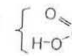
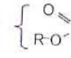
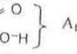
The GCA-EoS model was applied to multi component mixtures containing water, alcohols and any number of inert components by defining an unique associating group with two sites, the hydroxyl group OH, to represent association effects in these mixtures [3]. In this work the model is extended to mixtures containing, additionally, associating groups capable of forming dimers. Two new associating groups are defined as follows:

- the 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 an electropositive site.

Therefore the model is extended to mixtures containing three possible associating groups as described on Table 1. For each case, the fraction of non-bonded sites is obtained by solving the system of equations that result from equation 3.

The self and cross association models models are presented on Table 1.

Table 1: Self and cross association models defined in the GCA-EoS model.

Self-association			Assumptions	Association parameters
COOH	 A_1		$\Delta_{A_1A_1} \neq 0$	$\varepsilon_{A_1A_1}$ $\kappa_{A_1A_1}$
OH	O-H B_2 A_2		$\Delta_{A_2B_2} \neq 0$ $\Delta_{A_2A_2} = \Delta_{B_2B_2} = 0$	$\varepsilon_{A_2B_2}$ $\kappa_{A_2B_2}$
COOR	 A_3		$\Delta_{A_3A_3} = 0$	----
Cross-association				
OH-COOH	O-H B_2 A_2	A_1 	$\Delta_{A_1A_2} = \Delta_{A_1B_2} \neq 0$ $\Delta_{A_1A_1} \neq 0$ $\Delta_{A_2B_2} \neq 0$	$\varepsilon_{A_1A_2} = \varepsilon_{A_1B_2} = \frac{\varepsilon_{A_1A_1} + \varepsilon_{A_2B_2}}{2}$ $\kappa_{A_1A_2} = \kappa_{A_1B_2} = \sqrt{\kappa_{A_1A_1}\kappa_{A_2B_2}}$
OH-COOR	O-H B_2 A_2	A_3 	$\Delta_{B_2A_3} = \Delta_{A_3B_2} \neq 0$ $\Delta_{A_3A_2} = 0$	$\varepsilon_{A_3B_2}$ $\kappa_{A_3B_2}$
COOH-COOR	 A_1	A_3 	$\Delta_{A_1A_3} = \Delta_{A_3A_1} \neq 0$	$\varepsilon_{A_1A_3}$ $\kappa_{A_1A_3}$

PARAMETERIZATION

Association parameters

Self association

Following the procedure for the hydroxyl (OH) group [3], the COOH association parameters were determined by reproducing the fraction of non-bonded molecules predicted by the SAFT equation for linear acids from propanoic to decanoic at saturated liquid conditions.

Cross association

The cross association parameters between groups OH and COOH were calculated using the following combination rule between self association parameters:

$$\varepsilon_{COOH,OH} = \frac{\varepsilon_{COOH} + \varepsilon_{OH}}{2}$$
$$\kappa_{COOH,OH} = \sqrt{\kappa_{COOH}\kappa_{OH}} \tag{6}$$

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. It was decided to set them as adjustable parameters. The cross association parameters between the ester group and the OH group and between the ester and the acid group were estimated using low pressure vapor liquid equilibrium data (LPVLE) between esters and primary alcohols and between esters and acids, respectively. On Table 2 the corresponding self and cross-association parameters are presented.

Table 2: GCA-EOS self and cross association parameters.

Self association			
		$\varepsilon/k(K)$	$\kappa(cm^3/mol)$
COOH		6200.0	0.0200
OH		2700.0	0.8621
Cross association			
i	j	$\varepsilon_{ij}/k(K)$	$\kappa_{ij}(cm^3/mol)$
COOH	OH	4450.0	0.1313
	COOR	3000.0	0.9210
OH	COOR	2761.0	0.1574

Attractive parameters

The attractive term has 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 parameters α_{ij} and α_{ji}.). The new acid group was added to the GCA-EOS parameter table. Tables 3 and 4 show the pure-group and the binary interaction parameters, respectively. Also is included in both tables the source and type of experimental data used to fit the binary interaction parameters

Table 3: Pure group parameters

Pure group parameters						
Group	T_i^* (K)	q	g**	g'	g''	Experimental information
COOH	600	1.224	1217188	-0.111	0	P^{vap} [5] and LPVLE acids-alkanes[6]

Table 4: Binary interaction parameters

Binary interaction parameters						
i	j	k_{ij}	k'_{ij}	α_{ij}	α_{ji}	Experimental information
COOH	CH_3/CH_2	0.8472	0	0.1930	-0.4690	LPVLE acids-alkanes [6]
	CHOH	0.9726	0	11.693	3.8612	LPVLE acids-alcohols [7,8]
	CH_2OH	0.9477	0	10.117	1.9956	LPVLE acids-alcohols [7,8]
	CH_3OH	1.0369	0	0	0	LPVLE acids-alcohols [7,8]
	H_2O	1.0949	0	0	0	LPVLE acids-water [9,10]
	CH_3COO/ CH_2COO	1.0000	0	0	0	LPVLE acids-esters [6]
	CO_2	0.8651	0	-1.5043	-2.7738	HPVLE acids-CO_2 [11]
	TG	1.1000	0	0	0	γ^∞ [12]
CH_2COO	CH_2OH	1.0000	0	0	0	LPVLE alcohols-esters(2)
CH_3COO	H_2O	1.0700	0	0	0	LPVLE water-esters(2)
	CH_2OH	1.0000	0	0	0	LPVLE alcohols-esters(2)

RESULTS

Figures 1 to 4 show some of the correlation results obtained for several self and cross associating mixtures. The parameters obtained are used to predict high pressure phase equilibria in mixtures of supercritical gases with heavier components. On Figure 5 the VLE predictions for binary mixtures of ethane and octanol or nonanoic acid are presented. Figure 6 shows the model prediction for the binary VLE of several fatty acids in CO_2.

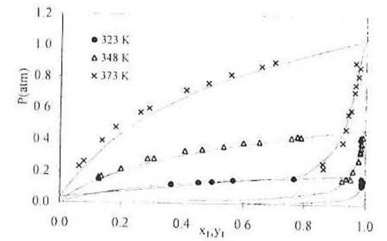


Figure 1: VLE of heptane(1)+pentanoic acid(2). Exp. Data: [6]; — GCA-EOS correlation.

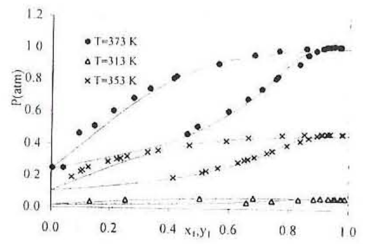


Figure 2: VLE of water(1)+propionic acid (2). Exp. Data: [9]; — GCA-EOS correlation.

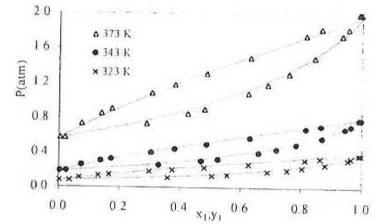


Figure 3: VLE of ethyl acetate(1)+acetic acid(2). Exp. Data: [6]; — GCA-EOS correlation.

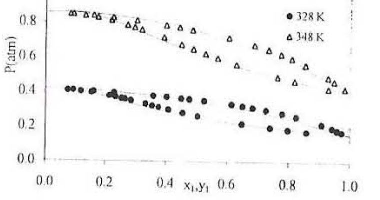


Figure 4: VLE of 1-propanol(1)+methyl propanoate(2).Exp.Data:[6];—GCA-EOS correlation.

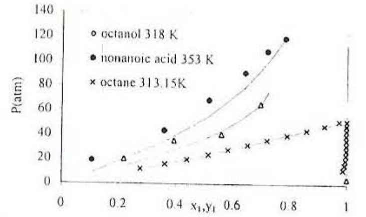


Figure 5: VLE of ethane (1)+several solutes (2) Exp. Data:[13]; — GCA-EOS prediction.

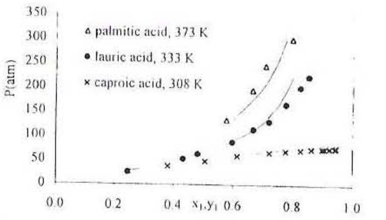


Figure 6: Binary VLE of CO_2 (1) and fatty acids (2): Exp. Data:[14,11]; — GCA-EOS prediction.

Finally, on Figure 7 the GCA-EOS predictions of high-pressure VLE for the ternary system CO2 + oleic acid + triolein are presented. As can be seen the model is able to correctly predict the higher affinity of CO_2 for the fatty acid.

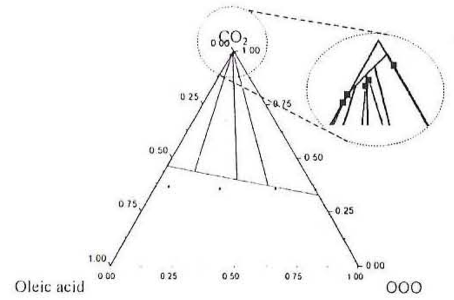


Figure 7: Ternary VLE of CO2+oleic acid+triolein. Exp.Data: [15]; — GCA-EOS prediction.

CONCLUSIONS

In this work, association effects in water, alcohols, carboxylic acids and esters were represented by a group contribution approach by defining three different association groups: the hydroxyl group, the acid group and the ester group. The parameters table obtained at low pressures (using binary mixtures of carboxylic acids, alcohols, esters, water and alkanes) and at high pressures (CO_2 and acids) was applied to mixtures of fatty acids and other fatty oil derivatives with supercritical fluids. Good results were obtained which suggest the use of the GCA-EOS as an engineering tool to optimize and design extraction and fractionation processes of fatty oil derivatives with supercritical fluids

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