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MODELING OF ASSOCIATION EFFECTS IN MIXTURES OF CARBOXYLIC ACIDS WITH ASSOCIATING AND NON-ASSOCIATING COMPONENTS

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***Abstract*-- The group contribution with association equation of state GCA-EOS has been applied to calculate thermodynamic properties of pure compounds and mixtures of carboxylic acids with paraffins, alcohols, water and gases, at low and high pressures. Two associating groups, OH and COOH, were defined. Self- and cross-association in these mixtures were quantified through two parallel COOH/COOH and OH/OH associations. The validity of this approach is supported by an excellent representation of pure compound properties (vapor pressures and compressibility factors) and phase equilibria in mixtures of (associating + inert) and (associating + associating) components at low and high pressures.**

***Keywords*-- Association, Group Contribution, Carboxylic acids.**

I. INTRODUCTION

Association and solvation effects, when present, play a major role in the properties of pure compounds and mixtures. They are particularly important in carboxylic acids, where association is present even at low vapor densities.

In the present work the group contribution with association equation of state GCA-EOS (Gros *et al.*, 1996) is applied to calculate phase equilibrium properties in mixtures of carboxylic acids, alcohols, water and gases, at low and high pressures.

The association term in the GCA-EOS model is based on Wertheim's theory for fluids with highly directed attractive forces as applied in the SAFT equation (Chapman *et al*, 1990), and follows a group contribution approach. Gros *et al.* (1996) have used a single hydroxyl (OH) associating group to represent association effects in alcohols, water and their mixtures. In this work the application of the GCA-EOS is extended to mixtures containing carboxylic acids, by defining a new COOH associating group. To allow a straightforward extension of the model to multicomponent mixtures containing OH and COOH associating groups, a new approach is proposed to solve the cross association problem.

II. SELF- AND CROSS-ASSOCIATION IN MIXTURES WITH CARBOXYLIC ACIDS

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 vapor phases. Generally only the formation of dimers is considered, and it is possible to find in the literature (Gmehling *et al*, 1982a) the values of the vapor phase dimerization constants for a number of carboxylic acids.

In order to model association by 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. The association strength is a function of two parameters: the volume (κ) and the energy (ε/k) of association. In this work a new associating group (COOH) was defined as having one associating site that self-associates by double hydrogen bonding (Fig. 1).

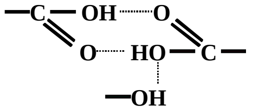

Fig.1. Schematic representation of self and cross association in carboxylic acids.

Following the procedure adopted by Gros *et al.* (1996) for the hydroxyl (OH) group, 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 (Wolbach and Sandler, 1997). The values obtained for the energy and volume of association were $\varepsilon/k^{COOH} = 6500K$ and $\kappa^{COOH} = 0.015\ cm^3/gmol$, respectively. As expected, the COOH energy of association is much larger than that of the OH group ($\varepsilon/k^{OH} = 2700K$), which is in accordance with the higher degree of association of carboxylic acids.

The extension of association theories to mixtures containing more than one associating compound requires the estimation of cross-association parameters and in some cases the numerical solution of a set of non-linear equations. Kraska (1998) presents a revision of the various rigorous and approximate solutions for cross-association models. Usually the problem is solved by setting some combination rule to evaluate the cross-association strength from the corresponding self-associations (in general geometric and/or arithmetic rules are applied) (Suresh *et al.*, 1992, Voutsas *et al.*, 1999).

The large difference between the energies of association of the COOH and OH groups precludes the use of this approach to evaluate cross-association effects in mixtures of carboxylic acids with water and/or alcohols. At room temperature, for example, the COOH self-association strength is ten thousand times that of the OH group. A mean value between such dissimilar quantities would be physically meaningless, and the cross-association strength calculated this way will tend to over-predict the degree of cross-association in a solution where the acid molecules are predominantly self-associated.

In this work a different empirical approach is proposed to evaluate cross-association in these mixtures. From the point of view of association, each carboxylic acid molecule is considered to have two associating groups: one COOH group which self-associates through a double hydrogen bonding, and a certain *fraction* of OH group that has a remnant association capacity and can self-associate with another OH group (see Fig. 1).

In this way, the cross association problem is replaced by the self-association between the OH group from the alcohol or water, and the *fraction* of OH group present in the carboxylic acid molecule. Following this methodology, the association of carboxylic acids and mixtures of carboxylic acids with water and/or alcohols is represented by two self-associations in parallel: COOH/COOH and OH/OH. The value of each self-association strength is calculated from the respective COOH and OH association parameters ($\varepsilon/k^{COOH} = 6500K$, $\kappa^{COOH} = 0.015$ cm^3/gmol, $\varepsilon/k^{OH} = 2700K$ and $\kappa^{OH} = 0.8621$ cm^3/gmol). The *fraction* of associating OH group provided by the carboxylic acid molecules was empirically determined by fitting vapor-liquid equilibrium (VLE) data on binary mixtures of acids with water and alcohols. A *fraction* of OH group equal to 0.25 gave the best correlation of these data.

The methodology proposed here has the additional advantage of solving the association problem by two explicit mathematical expressions for the fraction of non-bonded COOH and OH associating groups. This makes straight forward the application of the GCA-EOS model to multicomponent mixtures of carboxylic acids, water, alcohols and inert components.

III. ATTRACTIVE-ENERGY PARAMETERS

There are three contributions to the residual Helmholtz energy in the GCA-EOS model: free volume, attractive and associative contributions. The group-contribution 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 COOH functional group was not available in the GCA-EOS parameter table. In this work the attractive-energy parameters for this group and its interactions with the paraffinic (CH_3 and CH_2), alcohol (CHOH, CH_2OH, CH_3OH), water (H_2O), triglyceride (TG) and CO_2 functional groups were determined. Tables 1 an 2 show, respectively, the corresponding pure-group and binary interaction parameters. The experimental information used to fit these parameters include: vapor pressures (P^{vap}) of pure carboxylic acids; binary low-pressure vapor-liquid equilibria (LPVLE) for mixtures of carboxylic acids with alkanes, alcohols and water; high-pressure vapor-liquid equilibria (HPVLE) for binary mixtures of carboxylic acids with carbon dioxide; and infinite dilution activity coefficients (γ^∞) of alkanes in mixtures of triacetin with palmitic acid.

Table 1. Pure-group parameters

Group	T^* (K)	q	g^*	g’	g’’	Experimental information
COOH	600	1.224	1211745.4	-.1105	0.0	P^{vap} (1) and LPVLE acids-alkanes (2)

Source of data: (1) Daubert and Danner (1989); (2) Gmehling *et al.* (1982a)

Table 2. Binary interaction parameters

I	J	k_{ij}^*	k_{ij}’	α_{ij}	α_{ji}	Experimental information
COOH	CH_3	0.932	0.0	-2.946	-2.424	LPVLE acids-alkanes (2)
	CH_2	0.932	0.0	-2.946	-2.424	LPVLE acids-alkanes (2)
	CO_2	0.892	0.0	-2.370	-2.370	HPVLE acids-CO_2 (3)
	CHOH	1.069	0.0	2.366	-23.95	LPVLE acids-alcohols (4, 5)
	CH_2OH	1.096	0.0	2.366	-23.95	LPVLE acids-alcohols (4, 5)
	CH_3OH	1.150	0.0	2.366	-23.95	LPVLE acids-alcohols (4, 5)
	H_2O	1.140	0.0	18.66	4.000	LPVLE acids-water (6, 7)
	TG	1.062	0.0	0.0	0.0	$\gamma\infty$ (8)

Source of data: (2) Gmehling *et al.* (1982a); (3) Bharath *et al.* (1993); (4) Gmehling and Onken (1977a); (5) Gmehling *et al.* (1982); (6) Gmehling and Onken (1977); (7) Gmehling *et al.* (1998); (8) Bermudez *et al.* (2001)

IV. RESULTS AND DISCUSSION

The *correlation* of carboxylic acid vapor pressures gave an average relative error of 3% within a reduced temperature range between 0.55 and 0.90 (see Table 3). Table 4, on the other hand, compares experimental vapor compressibility factors (Z) at saturation (Miyamoto *et al.*, 1999) with GCA-EOS *predictions*. The low values of Z reflect the strong association of carboxylic acids in the vapor 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 showed by the experimental data.

Table 3: Pure-component vapor pressures.

Components	T(K)	Error %*
Acetic acid	325-545	3.28
Propanoic acid	325-565	1.46
Butanoic acid	350-530	1.72
Pentanoic acid	350-500	3.95
Hexanoic acid	370-550	2.53
Heptanoic acid	390-550	4.37
Octanoic acid	400-600	2.46
Nonanoic acid	500-630	3.57
Decanoic acid	450-630	4.31

*Error = $\sqrt{\sum\left[\left(P_{\exp}-P_{calc}\right)/P_{\exp}\right]^2}\ /\ NP$; NP: number of data points.

Table 4. Vapor phase compressibility factors

Component	T(K)	Z_{exp}	Z_{calc}	$\lvert\Delta Z\rvert / Z_{exp}$ (%)
Acetic acid	323.2	0.569	0.570	0.1
	343.2	0.579	0.580	0.1
	363.2	0.595	0.589	1.1
Propanoic acid	323.2	0.611	0.627	2.7
	343.2	0.627	0.638	1.8
	363.2	0.638	0.648	1.6
	383.2	0.664	0.657	1.1
Butanoic acid	343.2	0.687	0.723	5.2
	363.2	0.706	0.729	3.2
	383.2	0.720	0.734	2.0
	403.2	0.741	0.738	0.3
Pentanoic acid	363.2	0.793	0.826	4.1
	383.2	0.805	0.824	2.4
	403.2	0.807	0.823	2.0
	423.2	0.801	0.821	2.5

Figures 2 to 8 represent vapor-liquid equilibria (VLE) results for some binary mixtures of carboxylic acids with alkanes, carbon dioxide, alcohols and water. Excellent *correlation* (Fig. 2) and *prediction* (Fig. 3) of low- and high-pressure VLE were achieved for mixtures of alkanes with low and high molecular weight carboxylic acids. The same is true for mixtures with CO_2, as it can be inferred from the results shown in Fig. 4 (*prediction)* and Fig. 5 (*correlation*). Figs. 6 and 7 present some results from the *correlation* of vapor-liquid equilibria of cross associating mixtures.

Finally, Fig. 8 shows GCA-EOS *predictions* of high-pressure VLE for the ternary system CO2 + oleic acid + triolein. Even though the CO_2 solvent power predicted by the model is lower than the data measured by Bharath *et al.* (1992), the selectivity is correct; i.e. the equation shows the higher affinity of CO_2 for the fatty acid.

V. CONCLUSIONS

In this work, association effects in carboxylic acids were represented by a group contribution approach. Cross-association effects in mixtures of carboxylic acids with alcohols and water, were taken into account by solving two parallel self-association problems. With this approach and using a single set of parameters, good representation was obtained for pure component properties and phase equilibria in mixtures of carboxylic acids with inert compounds, alcohols and water at low and high pressures. The group contribution nature of the GCA-EOS allows it to be applied to mixtures for which experimental information is scarce or not available. In this respect, the GCA-EOS is a useful tool to explore process conditions for the extraction and fractionation of fatty acids and other fatty oil derivatives with supercritical fluids.

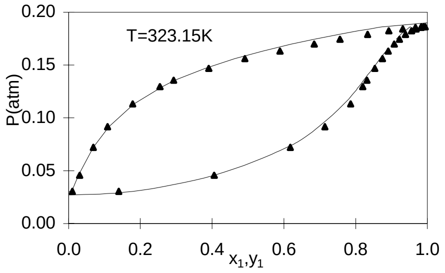

Fig. 2. VLE of heptane (1) + propanoic acid (2): ▲ Exp. (Gmehling *et al.*, 1982a, pg. 215); — GCA-EOS.

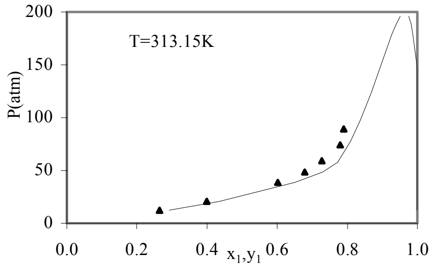

Fig. 3. VLE of ethane (1) + oleic acid(2): ▲ Exp.(Peter *et al.,* 1991); — GCA-EOS.

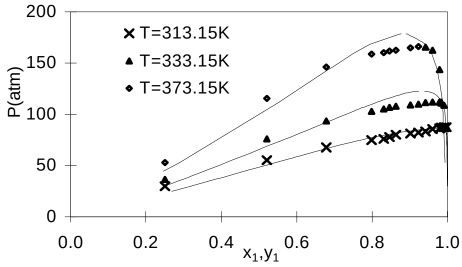

Fig. 4. VLE of CO_2 (1)+ butanoic acid (2): ● ▲ × Exp (Byun *et al.*, 2000), — GCA-EOS

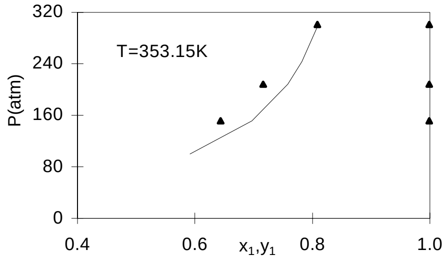

Fig. 5. VLE of CO_2 (1)+ palmitic acid(2): ▲ Exp. (Bharath *et al.,* 1993); — GCA-EOS.

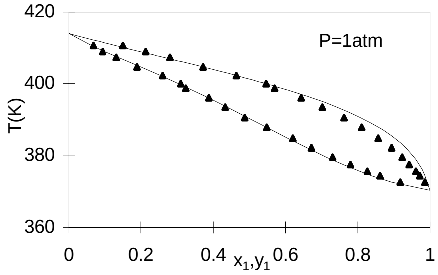

Fig. 6. VLE of 1-propanol (1)+ propanoic acid (2): ▲ Exp. (Gmehling *et al.*, 1982, pg.486); — GCA-EOS.

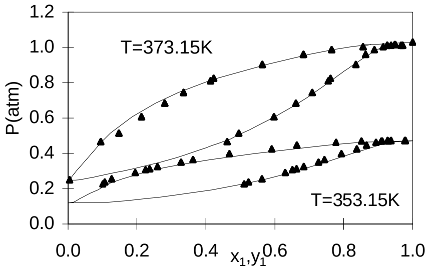

Fig. 7. VLE of H_2O (1)+ propanoic acid(2): ▲ Exp. (Gmheling and Onken, 1977a, pgs.222 and 224); — GCA-EOS.

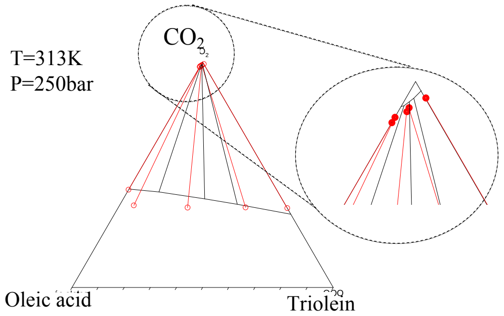

Fig. 8. VLE of the system CO2 + oleic acid + triolein: o ● Experimental (Bharath *et al*, 1992); — GCA- EOS

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APPENDIX

There are three contributions to the residual Helmholtz function (A^{res}) in the GCA-EoS model: free volume (A^{fv}), attractive (A^{att}) and associative (A^{assoc}).

$$A^{res} = A^{fv} + A^{att} + A^{assoc} \qquad \text{(A1)}$$

The free volume contribution is represented by the extended Carnahan-Starling equation for mixtures of hard spheres developed by Mansoori and Leland (1972):

$$(A/RT)^{fv} = 3\left(\lambda_1\lambda_2/\lambda_3\right)\left(\mathrm{Y}-1\right)+\left(\lambda_2^3/\lambda_3^2\right) \left(-Y+Y^2-\ln Y\right)+n\ln Y \qquad \text{(A2)}$$

with:

$$Y=\left(1-\frac{\pi\lambda_3}{6\mathrm{V}}\right)^{-1} \quad \text{and} \quad \lambda_k=\sum_i^{NC} n_i d_i^k$$

n_i being the number of moles of component i, NC the number of components in the mixture, n the total number of moles, V the total volume and d_i the hard-sphere diameter per mol of species i.

The following generalized expression gives the temperature dependence of the hard-sphere diameter:

$$d_i = 1.065655\, d_{ci}\{1-0.12\exp[-2T_{ci}/(3T)]\} \qquad \text{(A3)}$$

where d_{ci} and T_{ci} are, respectively, the critical hard-sphere diameter and critical temperature of component i. The value of d_{ci} can be determined from the critical properties:

$$d_{ci} = \left(0.08943RT_{ci}/P_{ci}\right)^{1/3} \qquad \text{(A4)}$$

or it can be calculated by fitting data on the vapor pressure of species i (Skjold-Jørgensen, 1984). For high molecular weight compounds (for which T_c and P_c are unknown and vapor pressure data is unavailable) the d_{ci} value can be determined by fitting experimental data on infinite dilution activity coefficients of alkanes in compound i (Bottini *et al.*, 1999).

The attractive contribution to the Helmholtz energy accounts for dispersive forces between functional groups, through a density-dependent, local-composition expression based on the NRTL model (Renon and Prausnitz, 1968):

$$(A/RT)^{att} = -\frac{z}{2}\sum_i^{NC} n_i \sum_j^{NG} v_j^i q_j \sum_k^{NG}\left(\theta_k g_{kj}\tilde{q}\,\tau_{kj}/RTV\right)/\sum_l^{NG}\theta_l\tau_{lj} \qquad \text{(A5)}$$

with:

$$\tilde{q} = \sum_i^{NC} n_i \sum_j^{NG} v_j^i q_j \qquad \text{(A6)}$$

$$\theta_j = \left(q_j/\tilde{q}\right)\sum_i^{NC} n_i v_j^i \qquad \text{(A7)}$$

$$\tau_{ij} = \exp\left(\alpha_{ij}\Delta_{ij}\tilde{q}/RTV\right) \qquad \text{(A8)}$$

$$\Delta g_{ij} = g_{ij} - g_{jj} \qquad \text{(A9)}$$

z being the coordination number (set equal to 10), v_j^i the number of groups of type j in molecule i, q_j the number of surface segments assigned to group j, $\tilde{q}$ the total number of surface segments, θ_k the surface fraction of group k, g_{ij} the attractive energy between segments of groups i and j, and α_{ij} the non-randomness parameter.

The attractive energy g_{ij} is calculated from the energy between like-group segments trough the following combination rule:

$$g_{ij} = k_{ij}\left(g_{ii}g_{jj}\right)^{1/2} \qquad \text{(A10)}$$

where the binary interaction parameter k_{ij} is symmetrical ($k_{ij} = k_{ji}$). Both, the attractive energy between like segments and the binary interaction parameter are temperature dependent:

$$g_{jj} = g_{jj}^*\left(1+g_{jj}'\left(T/T_j^*-1\right)+g_{jj}''\ln\left(T/T_j^*\right)\right) \qquad \text{(A11)}$$

$$k_{ij} = k_{ij}^*\{1+k_{ij}'\ln[2T/(T_i^*+T_j^*)]\} \qquad \text{(A12)}$$

where T_i^* is an arbitrary but fixed reference temperature for group i; g_{jj}^*, g_{jj}' and g_{jj}'' are pure-group energy parameters and k_{ij}^* and k_{ij}' are binary group interaction parameters.

The association contribution to the Helmholtz function is calculated with a group contribution expression (Gros *et al.*, 1996) based on Whertheim's theory (1984a,b, 1986a,b) of associating fluids:

$$\frac{A^{assoc}}{RT} = \sum_{i=1}^{NGA} n_i^{assoc}\left[\sum_{k=1}^{M_i}\left(\ln X^{(k,i)}-\frac{X^{(k,i)}}{2}\right)+\frac{1}{2}M_i\right] \qquad \text{(A13)}$$

where NGA represents the number of associating groups, n_i^{assoc} the number of moles of associating group i, M_i the number of associating sites assigned to group i and $X^{(k,i)}$ the mole fraction of group i not bonded at site k. The number of moles of associating group i is:

$$n_i^{assoc} = \sum_{m=1}^{NC} v_m^{i,assoc}\, n_m \qquad \text{(A14)}$$

where $v_m^{i,assoc}$ represents the number of times associating group i is present in molecule m and n_m is the total number of moles of species m; the summation includes all NC components in the mixture.

The mole fraction of group i not bonded at site k is determined from the following expression:

$$X^{(k,i)} = \left[1+\sum_{j=1}^{NGA}\sum_{l=1}^{M_j}\rho_j^{assoc}X^{(l,j)}\Delta^{(k,i,l,j)}\right]^{-1} \qquad \text{(A15)}$$

The value of $X^{(k,i)}$ depends on the molar density of associating group j ($\rho_j^{assoc} = n_j^{assoc}/V$) and the association strength $\Delta^{(k,i,l,j)}$ between site k of group i and site l of group j:

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)}\left[\exp\left(\varepsilon^{(k,i,l,j)}/kT\right)-1\right] \qquad \text{(A16)}$$

where the association parameters are the energy (ε) and volume (κ) of association. In mixtures containing alcohols and/or water, association effects can be computed by the same hydrogen-bonding hydroxyl group characterized by an energy ε/k = 2700 K and a volume κ = 0.8621 cm^3/mol (Gros *et al.*, 1997).

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