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.
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 and
$\kappa$).

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$_2$OH,
CH$_3$OH), water (H$_2$O), triglyceride (TG) and CO$_2$
functional groups were determined. Tables 1 and 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 ($\gamma_\infty$) of alkanes in
mixtures of triacetin with palmitic acid.

### 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
randomness parameters $\alpha_{ij}$ and $\alpha_{ji}$).

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mixtures of carboxylic acids with carbon dioxide; and
infinite dilution activity coefficients ($\gamma_\infty$) of alkanes in
mixtures of triacetin with palmitic acid.

#### Table 1. Pure-group parameters

<table>
<thead>
<tr>
<th>Group</th>
<th>$T^*$ (K)</th>
<th>$q$</th>
<th>$g^*$</th>
<th>$g'$</th>
<th>$g''$</th>
<th>Experimental information</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
<td>600</td>
<td>1.224</td>
<td>1211745.4</td>
<td>-1.105</td>
<td>0.0</td>
<td>P$_{vap}$ (1) and LPVLE acids-alkanes (2)</td>
</tr>
</tbody>
</table>

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

#### Table 2. Binary interaction parameters

<table>
<thead>
<tr>
<th>I</th>
<th>J</th>
<th>$k_{ij}^*$</th>
<th>$k_{ij}'$</th>
<th>$\alpha_{ij}$</th>
<th>$\alpha_{ji}$</th>
<th>Experimental information</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
<td>CH$_3$</td>
<td>0.932</td>
<td>0.0</td>
<td>-2.946</td>
<td>-2.424</td>
<td>LPVLE acids-alkanes (2)</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>0.932</td>
<td>0.0</td>
<td>-2.946</td>
<td>-2.424</td>
<td>LPVLE acids-alkanes (2)</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.892</td>
<td>0.0</td>
<td>-2.370</td>
<td>-2.370</td>
<td>HPVLE acids-CO$_2$ (3)</td>
<td></td>
</tr>
<tr>
<td>CHOH</td>
<td>1.069</td>
<td>0.0</td>
<td>2.366</td>
<td>-23.95</td>
<td>LPVLE acids-alcohols (4, 5)</td>
<td></td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>1.096</td>
<td>0.0</td>
<td>2.366</td>
<td>-23.95</td>
<td>LPVLE acids-alcohols (4, 5)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>1.150</td>
<td>0.0</td>
<td>2.366</td>
<td>-23.95</td>
<td>LPVLE acids-alcohols (4, 5)</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.140</td>
<td>0.0</td>
<td>18.66</td>
<td>4.000</td>
<td>LPVLE acids-water (6, 7)</td>
<td></td>
</tr>
<tr>
<td>TG</td>
<td>1.062</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>$\gamma_\infty$ (8)</td>
<td></td>
</tr>
</tbody>
</table>

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.

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

*Error = \( \sqrt{\frac{\sum (P_{exp} - P_{calc})^2}{NP}} \); NP: number of data points.

Table 4. Vapor phase compressibility factors

| Component     | T(K) | Z_{exp} | Z_{calc} | |ΔZ| / 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 CO₂, 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 CO₂ 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 CO₂ 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 CO₂ (1) + butanoic acid (2): × × × × Exp (Byun et al., 2000), — GCA-EOS

Fig. 5. VLE of CO₂ (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 H₂O (1) + propanoic acid (2): ▲ Exp. (Gmehling 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

REFERENCES
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Byun, Hun-soo, Nam-seok Jeon and M.A. McHugh, “Phase behavior and modeling of supercritical carbon dioxide - acid mixtures”, *Proc. 5th Int. Symposium on Supercritical Fluids* (CD-ROM), Atlanta, Georgia, USA, (2000).


**APPENDIX**

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

$$A^{res} = A^f + A^a + A^{assoc} \quad (A1)$$

The free volume contribution is represented by the extended Carnahan-Starling equation for mixtures of hard spheres developed by Mansoori and Leland (1972):
\[(A/RT)^{TV} = 3\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3}\right) \left(-Y + 2 - \ln Y\right) + n \ln Y\]  
(A2)

with:

\[Y = \left(1 - \frac{\pi d_i^3}{6V}\right)^{-1}\]

\[\lambda_k = \sum_i n_i d_i^k\]

\[n_i\] 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:

\[d_i = 1.065655 d_{ci}[1 - 0.12 \exp(-2 T_{ci}/3T)]\]  
(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:

\[d_{ci} = (0.08943RT_{ci}/P_{ci})^{1/3}\]  
(A4)

or it can be calculated by fitting data on the vapor pressure of species \(i\) (Skjold-Jorgensen, 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):

\[\frac{(A/RT)^{att}}{ RT} = \frac{z}{2} \sum_{i,j} n_i n_j \sum_{k} (\theta_k g_{ij} \tilde{q} \tau_{ij} / RTV) / \sum_k \theta_k \tau_{ij}\]  
(A5)

where:

\[\tilde{q} = \sum_i n_i \sum_j v_{ij} \tilde{q}_j\]  
(A6)

\[\theta_j = \left(\tilde{q}_j / \tilde{q}\right) \sum_i n_i v_{ij}\]  
(A7)

\[\tau_{ij} = \exp(\Delta g_{ij} \tilde{q} / RTV)\]  
(A8)

\[\Delta g_{ij} = g_{ij} - g_{ij}\]  
(A9)

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

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

\[g_{ij} = k_q \left(g_{ij} g_{ij}\right)^{1/2}\]  
(A10)

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

\[g_{ij} = g_{ij}^* \left[1 + g_{ij}^* \left(T/T_i^* - 1\right) + g_{ij}^* \ln(T/T_i^*)\right]\]  
(A11)

\[k_{ij} = k_{ij}^* \left[1 + k_{ij} \ln(2T_i^* / T_j^*)\right]\]  
(A12)

where \(T_i^*\) is an arbitrary but fixed reference temperature for group \(i\); \(g_{ij}^*\), \(g_{ij}^*\) and \(g_{ij}^*\) 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:

\[\frac{\Delta_{assoc}^{RT}}{RT} = \sum_{i=1}^{NGA} n_i^{assoc} \sum_{j=1}^{M_i} \ln \left(X^{(i,j)} - X^{(i,j)} \right) + \frac{1}{2} M_i \]  
(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 \(X^{(i,j)}\) the mole fraction of group \(i\) not bonded at site \(k\).

The number of moles of associating group \(i\) is:

\[n_i^{assoc} = n_m \sum_{m=1}^{v_{i,m,assoc}} n_m\]  
(A14)

where \(v_{i,m,assoc}\) 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:

\[X^{(i,k)} = \left[1 + \sum_{j=1}^{NGA^{M_i}} \sum_{l=1}^{\rho_{j,assoc}} X^{(l,j,i)} \Delta^{(k,l,j,i)} \right]^{-1}\]  
(A15)

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

\[\Delta^{(k,l,j,i)} = e^{\left(U^{(i,j,d,i)} / kT\right) - 1}\]  
(A16)

where the association parameters are the energy \((e)\) and volume \((\kappa)\) 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 \(e/k = 2700\) K and a volume \(\kappa = 0.8621\) cm\(^3\)/mol (Gros et al., 1997).

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