

# 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.

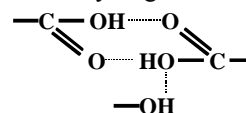
In the present work the group contribution with association equation of state GCA-EOS (Gros *et al.*, 1996) is applied to calculate phase equilibrium properties in mixtures of carboxylic acids, alcohols, water and gases, at low and high pressures.

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 ( $\kappa$ ) and the energy ( $\epsilon/k$ ) 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  $\epsilon/k^{\text{COOH}} = 6500\text{K}$  and  $\kappa^{\text{COOH}} = 0.015 \text{ cm}^3/\text{gmol}$ , respectively. As expected, the COOH energy of association is much larger than that of the OH group ( $\epsilon/k^{\text{OH}} = 2700\text{K}$ ), 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-