# A GENERAL GROUP CONTRIBUTION MODEL FOR ACTIVITY COEFFICIENTS IN ASSOCIATING SOLUTIONS

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## Abstract

A modified UNIFAC group contribution model for the prediction of activity coefficients in associating mixtures was proposed recently (Mengarelli *et al*, 1999). In the present work the model is extended to carboxylic acids by defining a general associating group which allows a straightforward extension to multicomponent mixtures. The residual UNIFAC local composition term is re-parameterized in order to take into account only dispersive forces between associating and inert functional groups. Good correlation and prediction of experimental VLE, LLE and $\gamma^{\infty}$ data for mixtures containing water, acids, alcohols and inert compounds are obtained.

## Introduction

A modified UNIFAC model that takes into account association effects was presented previously (Mengarelli *et al*, 1999). This model results from adding an association term to the traditional UNIFAC residual and combinatorial contributions to the activity coefficients. The association term is based on Wertheim's theory for fluids with highly directed attractive forces (Wertheim, 1984a,b; 1986a,b) following the group contribution approach proposed by Gros *et al.* (1996) in the GCA-EOS model. This model was applied to mixtures containing alcohols and water by defining the same hydroxyl OH associating group. This approach allows a straightforward extension to multicomponent mixtures. In this way, the cross-association in mixtures of alcohols, water and inert components is treated as a self association problem, which has an explicit solution for the activity coefficients as a function of the global mixture composition.

In this work, the association model (A-UNIFAC) is applied to mixtures containing also carboxylic acids. Moreover, in order to improve the LLE predictions, the number of alkane groups is increased, by introducing a water soluble (WS)$CH_2$ group.

To model the association behavior of the carboxylic acids it is necessary to define its associating group and the corresponding number of sites. This family of compounds presents a high degree of association in both liquid and vapor phases and, usually, it is defined an associating group COOH with one associating site, representing the formation of dimers. In the vapor phase the carboxylic acids behavior strongly differs from water and alcohols, as they associate even at very low vapor densities. However, at high liquid densities, all these compounds present a high and similar degree of association.

Fig. 1 represents the fraction of non bonded sites calculated by the SAFT equation (Huang and Radosz, 1990) for ethanol and acetic acid at saturated liquid conditions. At the high temperature region, where the liquid phase density decreases towards the critical density value, the ethanol and acetic acid curves diverge. But, away from the critical region or at low reduced temperatures, in high liquid density conditions both compounds show the same degree of association. Apparently for these conditions it would be possible to represent association effects of acids using the same association model of water and alcohols.