Extension of UNIFAC to associating systems

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Abstract. An extended UNIFAC group contribution model for the prediction of activity coefficients in associating mixtures was presented recently (Mengarelli et al., 1999). In the present work the model is applied to solutions containing alcohols, water carboxylic acids and inert components. 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 representation of vapor-liquid and liquid-liquid equilibrium, as well as infinite dilution activity coefficients is achieved by using a single set of group interaction parameters.

Keywords: Activity coefficient, Association, Group contribution.

1. Introduction

A modified UNIFAC model that takes into account association effects was presented previously (Mengarelli *et al*, 1999). This model was derived by 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) and it follows the group contribution approach proposed by Gros *et al.* (1996) in the GCA-EOS model. This model was successfully applied to represent phase equilibria in mixtures containing alcohols and water, by using the same hydroxyl OH associating group, to take into account hydrogen bonding in all alcohols and water. With this approach it was possible to solve the self- and cross-association problem present in multicomponent mixtures of alcohols, water and inert components, by solving a self-association problem that has an explicit solution for the activity coefficients as a function of the global mixture composition.

The purpose of this work is to apply this association model (A-UNIFAC) to mixtures containing carboxylic acids. It is known that carboxylic acids show a high degree of association even at low vapor densities and it is generally accepted the formation of dimers in both, liquid and vapor phases. Even though the association of carboxylic acids in the vapor phase strongly differs from that of water and alcohols, all these compounds present a high degree of association at high liquid densities.

Fig. 1 shows the fraction of non bonded sites calculated by the SAFT equation (Huang and Radosz, 1990) for ethanol and acetic acid at saturated liquid conditions. It can be seen that the ethanol and acetic acid curves diverge at the higher temperatures; i.e., when the liquid phase density decreases towards the critical density value. But both compounds show the same degree of association at low temperatures, high liquid density conditions. This suggests that association effects in carboxylic acids liquid solutions away from the critical region or at low reduced temperatures could in principle be treated by the same hydrogen bonding association model applied to alcohols and water.