GROUP CONTRIBUTION MODELING OF ACTIVITY COEFFICIENTS IN ASSOCIATING SOLUTIONS CONTAINIG WATER, ALCOHOLS AND CARBOXYLIC ACIDS

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Abstract. A modified UNIFAC group contribution model for the prediction of activity coefficients in associating solutions (A-UNIFAC) is applied to calculate phase equilibria in binary and ternary mixtures of associating and non-associating species, including alcohols, water, carboxylic acids, esters, alkanes, aromatic hydrocarbons and alkyl chlorides. Self- and cross-association in these mixtures is adequately described by the definition of a single hydrogen-bonding group. The new model is able to give good predictions of vapor-liquid equilibria, liquid-liquid equilibria and infinite dilution activity coefficients, using a single set of group-interaction parameters.

Keywords: Activity coefficient, Association, Group contribution.

1. Introduction

Association and solvation effects, when present, have a major contribution to the properties of solutions. The modeling of activity coefficients in these solutions represents a difficult problem, particularly for the highly non-ideal mixtures between associating and non-polar species. Traditional thermodynamic models, such as UNIFAC, ASOG, UNIQUAC, NRTL, etc., have difficulties in representing adequately the activity coefficients of these solutions in all the range of compositions, from infinite dilution to high concentrations of the associating component.

Mengarelli et al. (1999) have recently presented a modified UNIFAC model that takes into account association effects. This model adds an association term to the original UNIFAC combinatorial and residual expressions (Fredenslund et al., 1975). 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 Zabaloy et al. (1993) and Gros et al. (1996) in the GCA-EOS equation. This extended UNIFAC model has been successfully applied to represent phase equilibria in mixtures containing alcohols, water and inert components (Ferreira et al, 1999). A single hydrogen-bonding hydroxyl (OH) group was used in these papers to calculate association effects in all alcohols and water. This approach allows self- and cross-associations to be represented as a single self-association problem, with an explicit mathematical solution for the fraction of non-bonded molecules. In the present work this UNIFAC association model (A-UNIFAC) is applied to calculate activity coefficients in mixtures containing alcohols, water, carboxylic acids, esters, alkanes, aromatic hydrocarbons and alkyl chlorides.