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Fluid Phase Equilibria 227 (2005) 165–176
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Extension of the A-UNIFAC model to mixtures of cross- and self-associating compounds

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Received 18 February 2004; received in revised form 10 November 2004; accepted 12 November 2004

Abstract

In the present work an extended UNIFAC group contribution model is used to calculate activity coefficients in solutions containing alcohols, water, carboxylic acids, esters, alkanes and aromatic hydrocarbons. The limiting expressions for the association contribution to the activity coefficients at infinite dilution are presented and discussed. A new set of interaction parameters between associating and non-associating functional groups is reported. This set of parameters is applied in the association model to predict vapor–liquid, liquid–liquid equilibrium and infinite dilution activity coefficients.

Keywords: Model; Activity coefficients; Association; Group-contribution

1. Introduction

Mengarelli et al. [1] presented a modified UNIFAC model that takes into account association effects in the computation of liquid-phase activity coefficients. This model adds an association term to the original UNIFAC combinatorial and residual expressions [2,3]. The association term is based on Wertheim's theory for fluids with highly directed attractive forces [4–7] and it follows the group contribution approach proposed by Zabaloy et al. [8] and Gros et al. [9] in the GCA-EoS equation. A single hydroxyl (OH) hydrogen-bonding group, the same for all alcohols and water, was used to calculate association effects. This approach allowed self- and cross-associations to be solved as a single self-association problem for the alcohols and alcohols + water systems, with an explicit mathematical solution for the fraction of non-bonded OH groups.

In the present work this UNIFAC association model (A-UNIFAC) is extended for the calculation of activity coefficients in mixtures containing alcohols, water, carboxylic acids, esters, aromatic hydrocarbons and alkanes.

2. Association term in the A-UNIFAC model

The mechanism of association in Wertheim's perturbation theory is determined by the number of bonding sites assigned to each associating molecule. For example, a one-site association model describes dimerization of carboxylic acids, while a two-site model is required to represent the formation of higher oligomers in alcohols. Similarly, in group-contribution association models [1,9] the number of bonding sites in each functional group determines the type of association. The general expression for the association activity coefficient term (γ^{assoc}), which is derived from the association residual Helmholtz energy [10–12], is a function of the fraction of non-bonded sites in the solution (X^{A_k}) and in

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doi:10.1016/j.fluid.2004.11.009