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Modelling of phase equilibria for associating mixtures using an equation of state

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Abstract

In the present work, the group contribution with association equation of state (GCA-EoS) is extended to represent phase equilibria in mixtures containing acids, esters, and ketones, with water, alcohols, and any number of inert components. Association effects are represented by a group-contribution approach. Self- and cross-association between the associating groups present in these mixtures are considered. The GCA-EoS model is compared to the group-contribution method MHV2, which does not take into account explicitly association effects. The results obtained with the GCA-EoS model are, in general, more accurate when compared to the ones achieved by the MHV2 equation with less number of parameters. Model predictions are presented for binary self- and cross-associating mixtures.

Keywords: Phase equilibria; Equation of state; Group-contribution model; Association

1. Introduction

The group contribution with association equation of state (GCA-EoS) was initially proposed by Gros *et al.* [1]. It results from the addition of a third contribution, which quantifies the association forces, to the original repulsive and attractive terms of the group-contribution equation of state, GC-EoS [2,3].

The GCA-EoS was successfully applied to multicomponent mixtures containing water, alcohols, and any number of inert components by defining a single associating group, the hydroxyl group OH, to represent association effects in these mixtures [1]. This approximation resulted in very good representation of the thermodynamic properties and phase equilibria for solutions containing these associating components [1,4].

In this work, the GCA-EoS is extended to several cross-associating mixtures containing esters, ketones, alcohols, water, acids, aromatics, and alkanes. The parameterization strategy is described, followed by the presentation of correlation and prediction results obtained with the GCA-EoS. A comparison with the group-contribution equation of state based on the modified Huron–Vidal second order mixing rule (MHV2) [5,6] is made.

2. The group contribution with association equation of state

The total Helmholtz energy can be written as a sum of three terms

$$A = A^{rep} + A^{attr} + A^{assoc}. \quad (1)$$

The repulsive term is described by the Mansoori and Leland expression for hard-spheres [7] and the attractive

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