APPLICATION OF THE GCA-EOS MODEL TO THE SUPERCRITICAL PROCESSING OF ASSOCIATING OIL DERIVATIVES: FATTY ACIDS, ALCOHOLS AND TRIGLYCERIDES

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Supercritical processes are of interest in the fatty oil industry for a variety of applications: extraction and refining, removal of pollutants, recovery of specialties, hydrogenation of oils and derivatives, etc.

Typical process mixtures include heavy compounds and gases at near-critical conditions. At high pressures these asymmetric systems present a complex multi-phase behavior, difficult to model. This complexity increases if some of the mixture components are able to self- and/or cross associate.

In the present work, the group contribution with association equation of state (GCA-EOS) [3] is extended to represent high pressure phase equilibria in mixtures of supercritical gases (carbon dioxide, propane, ethane) with fatty oil derivatives, such as mono- and di-glycerides, fatty acids, alcohols, water and esters. Self- and cross-association between the associating groups present in these mixtures are considered.

Satisfactory correlation and prediction of equilibrium data are obtained. The capacity of the model to follow the behavior of the solutions towards the limit at infinite dilution of the associating components is of particular importance.

INTRODUCTION

Association and solvation effects have a major role in the properties of pure compounds and mixtures that can form hydrogen bonds. The group contribution with association equation of state GCA-EOS [3] explicitly takes into account those strong and highly directed attractive forces in its group contribution association term, which is based on Wertheim's theory as applied in the SAFT equation [4]. A single hydroxyl (OH) associating group was used to represent association effects in alcohols, water and any number of inert components [3]. In this work the GCA-EOS model is extended to mixtures containing additionally carboxylic acids and esters by defining two new associating groups: the COOH and COOR groups.

THE GCA-MODEL

The GCA-EOS results from the addition of a third term, which quantifies the association forces, to the original repulsive and attractive terms of the group contribution equation of state, GC-EOS [2]. The expression for the association term of the residual energy of Helmholtz is a function of the number of association groups NGA present in the mixture: