

THE EXTENDED GCA-EOS MODEL FOR MIXTURES OF FATTY OILS AND DERIVATIVES

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Abstract: *The Group Contribution Equation of State GC-EOS has been satisfactorily applied to the modeling of high-pressure phase equilibria of supercritical gases (CO₂, propane, ethane, dimethylether) with pure triglycerides and natural vegetable oils. The GC-EOS model size-related parameter, i.e. the critical hard sphere diameter, of the high molecular weight compounds were determined by fitting infinite dilution activity coefficients (γ^∞) of n-alkanes in these heavy compounds. In this way the GC-EOS model was able to correlate and predict vapor-liquid (VLE) and liquid-liquid (LLE) equilibria of these mixtures, using a unique set of parameters, in good agreement with experimental data. In this work the application of the model is extended to mixtures containing fatty oil derivatives, such as fatty acids, fatty acids esters, mono - and diglycerides. The associating effects between molecules are described using an upgraded version of the model, the Group Contribution Associating - EOS. Satisfactory correlation and prediction of experimental VLE, LLE and γ^∞ data in binary and ternary mixtures of these products with supercritical gases are obtained.*

Keywords: *Fatty acid, Group contribution, Triglycerides, Equations of State*

1. INTRODUCTION

There is a great variety of potential applications of supercritical fluids for the purification and refining of natural oils and derivatives. A recent compilation on this subject has been given by King and List (1996). The analysis of these processes requires reliable predictive methods for phase equilibrium calculations in mixtures of high-molecular weight triglycerides and derivatives with low-molecular weight solvents.

Previous work [Bottini *et al.*, 1999; Florusse *et al.*, 1999; Fornari *et al.*, 1999] has shown the capability of the GC-EOS developed by Skjold-Jorgensen (1984) to describe simultaneously, i.e. with the same set of parameters, the VLE and LLE observed in supercritical gases + vegetable oil mixtures. The group contribution approach makes possible to characterize, by the definition of pseudo-components and using a few number of functional groups, a large number of saturated and unsaturated oils and derivatives. The parameterization was made taking into account:

- The definition of a triglyceride TG [(CH₂COO)₂(CHCOO)] group to characterize compounds derived from the triple esterification of glycerol. Pure group parameters for the TG group, and binary interaction parameters between this group and various functional