GCA-EOS modeling of mono- and di-carboxylic acids for phase equilibria prediction by group contribution

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Carboxylic acids are present in a wide range of industrial processes, including the production of nylon, biodegradable plastics, soaps and detergents, and pharmaceuticals. Low molecular weight carboxylic acids appear frequently in a number of industrially important waste streams, from which they must be recovered, preventing pollution and generating a profit. On the other hand, high molecular weight carboxylic acids (i.e. fatty acids) derived from fats and oils, are used in the production of coverings, surfactants, plastics, and cleaning products. Dicarboxylic acids are also industrially important compounds. Their versatile properties make them important ingredients in the manufacture of various commodity and specialty chemicals. Moreover, the increased interest in biomass processing, enhances the role of dicarboxylic acids, such as succinic, adipic and itaconic acids, and other polyfunctional acids such as levulinic and lactic acids, as building blocks for the chemical industry of the future [2–4].

Crystallization and extractive crystallization processes are often applied to separate mixtures containing dicarboxylic and fatty acids. Therefore, not only the knowledge of fluid phase behavior is needed for process design, but also is key the prediction of solid phase precipitation. Various approaches have been used in the literature to describe carboxylic acid mixtures. These include classical thermodynamic models, like activity coefficient models and cubic equations of state (EOS). Generally, when dealing with the vapor-liquid equilibria (VLE), classic models fail describing the vapor phase due to the dimerization of low molecular

weight acids, even at low pressure, attributed to the formation of strong hydrogen bonds. In this regard, advanced EOSs that explicitly consider hydrogen bond formation offer a clear advantage over classical models. Most of these models belong to the SAFT family [5], and many authors [6–9] focused the discussion on the best association scheme for carboxylic acids, modeling these mixtures with the scheme 1A (one single site, able to cross and self-associate), scheme 2B (one negative and one positive sites), and more complex approaches combining the both schemes. In general, the conclusion is that the association scheme 1A offers the best performance taking into account a trade-off between precision and simplicity.

The aim of this work is to develop a thermodynamic model capable of predicting the phase behavior of mixtures containing a variety of organic acids, mono- and poly-functional, under a wide range of conditions and considering multiphase equilibrium types. In this sense, a group contribution (GC) approach model allows predicting phase behavior of systems for which experimental information is scarce or not available, such as complex molecules derived from bioresources. In this work, we extend the Group Contribution with Association EOS (GCA-EOS) [10] to model fluid-fluid and solid-fluid equilibria in mixtures containing mono- and dicarboxylic acids with alkanes, alkenes, cycloalkanes and water. We show that GCA-EOS predicts phase behavior of these complex mixtures without introducing "second order" groups or other type of correctios that distort the GC approach.

1. References

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