AN ASSOCIATION UNIFAC MODEL FOR AQUEOUS AND ALCOHOL SOLUTIONS OF SUGARS

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SUMMARY

In this work, a modified UNIFAC model [1] that explicitly takes into account association effects is applied to mixtures containing common sugars, alcohols and water.

Following the same strategy adopted before [2], four residual groups were defined to represent the sugars family: the pyranose ring (PYR), the furanose ring (FUR), the osidic bond (-O-) and the hydroxyl ring group (OH_{ring}) [2]. For the association term, a general two sites OH associating group is used to represent association effects in these solutions, allowing a straightforward extension to multicomponent mixtures. Correlation of both solvent activity properties (water activities, vapor pressures, boiling and freezing points of aqueous D-glucose and D-fructose solutions) and sugars (D-fructose, D-glucose and sucrose) solubility in water, ethanol and methanol give very good results. Satisfactory predictions are obtained for vapor-liquid equilibrium and solid-liquid equilibrium of ternary and quaternary mixtures of sugars in mixed solvents.

INTRODUCTION

The UNIFAC group contribution method has been used for the prediction of thermodynamic properties of mixtures containing sugars and polar solvents like water and alcohols [2-9].There is one UNIFAC model that explicitly takes into account hydrogen bonding: the physical chemical UNIFAC developed by Catté and coworkers [8], for aqueous solutions of sugars. The authors introduce a chemical part to model conformational and solvation equilibria between water and sugars. The physical part is given by the modified UNIFAC model proposed by Larsen et al. [10]. However, the fact that there is neither enough available information for the conformers composition in wide ranges of temperature, nor about the influence on that equilibrium of more than one solvent or sugar in the solution, makes the use of this method very difficult.

In this work, a modified UNIFAC model [1] is applied. This model was derived by adding an association term to the traditional UNIFAC residual and combinatorial contributions to the activity coefficients. The group association term is based on the Wertheim's theory for fluids with highly directed attractive forces [11-14]. This model was successfully used for the representation of phase equilibria in mixtures containing alcohols and water, by using the same hydroxyl OH associating group, to take into account hydrogen bonding in all alcohols and water. With this approach it is possible to solve the self- and cross-association problem present in multicomponent mixtures of alcohols, water and inert components, by solving a self-association problem that has an explicit solution for the activity coefficients as a function of the global mixture composition.

THE A-UNIFAC MODEL

a. Association term

It is known that sugars form hydrogen bonding with water and alcohols. In order to limit the