Phase Equilibria in Sugar Solutions Using the A-UNIFAC Model

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In this work, a modified UNIFAC model that explicitly takes into account association effects is used to describe the thermodynamic properties of phase equilibria of mixtures containing common sugars, alcohols, and water. Three main groups were defined to represent the sugars family: the sugar ring (pyranose and furanose), the osidic bond (−O−), and the hydroxyl ring group (OH_{ring}). For the association term, a general two-site OH associating group is used to represent association effects in these solutions, allowing a straightforward extension to multicomponent mixtures. Correlation of both solvent properties (osmotic coefficients, water activities, vapor pressures, and boiling and freezing points of binary aqueous sugar solutions) and sugar solubility in water and alcohols gives very accurate results. Good predictions are obtained for vapor−liquid equilibrium and solid−liquid equilibrium of ternary and quaternary mixtures of sugars in mixed solvents.

Introduction

Carbohydrates are one of the most abundant classes of organic compounds that can be found in living organisms. This large natural resource has a broad range of applications in the chemical industry. They are present in a variety of industries (textile, paper, coatings, and food) and are, also, used in several biological applications. In this work, the focus is on the important fraction of carbohydrates made up of the smaller building units: the mono- and disaccharides and their phase behavior in solvents such as water or alcohols.

In the past decade, a small number of models were specially developed or applied to the description of the phase equilibria of sugar mixtures. Some authors used a molecular approach, e.g., the Peng−Robinson equation of state[1] or the modified UNIQUAC model.[2,3] The majority of the models, however, follows a group contribution approach, mainly because of their predictive nature. The modified UNIFAC model[4] was used to predict the water activity, boiling temperature, and freezing temperature of aqueous solutions of sugars using the already defined UNIFAC groups.[5] To do this, the authors have used the existing groups (CH_2, CH, C, OH, CHO, and H_2O) and the corresponding parameters table. However, this model cannot correctly predict properties that depend on the activity coefficient of the solute and does not distinguish the differences between carbohydrate isomers (e.g., fructose, glucose, galactose, etc.). This suggests the introduction of new main groups to represent sugar molecules. The UNIFAC model[6] was applied to sugar aqueous mixtures by introducing three new different groups to represent sugar molecules.[7,8] Another model based on the modified UNIFAC method[4] was proposed: the P&M UNIFAC.[9] Four new main groups were introduced: the pyranose ring (PYR), the furanose ring (FUR), the hydroxyl group directly attached to the ring (OH_{ring}), and the osidic bond (−O−)

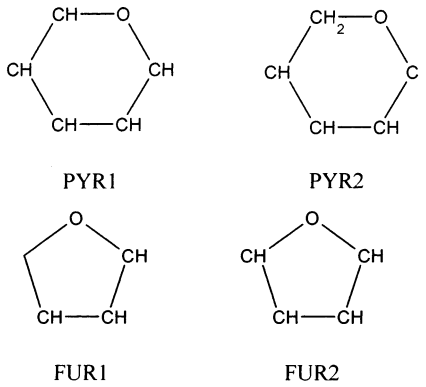

Figure 1. UNIFAC subgroups to represent sugar molecules.[13]

(see Figure 1). More recently, the S-UNIFAC model was presented.[10] The liquid−liquid equilibria table of parameters of the UNIFAC model is used.[11] In this case, two new main UNIFAC groups were introduced to represent sugars: $CHOH_{sugar}$ and the group CH−O−CH for the disaccharide osidic bond. Besides the interaction parameters, additional parameters were estimated: a different group area Q parameter was used in the combinatorial and residual terms. All of the above-mentioned UNIFAC models use the symmetric convention for the activity coefficients. Another modified UNIFAC model[4] was developed to represent the activity coefficients of biochemicals in water, including sugars: the Bio-UNIFAC model.[12] However, this model is based on the asymmetrical convention for activity coefficients. Besides the introduction of new UNIFAC groups to represent sugars, some authors have introduced other modifications, to take into account the existence of specific hydrogen-bonding interactions. This is the case of a physical chemical UNIFAC model developed for aqueous solutions of sugars.[13] The physical part is given by the modified UNIFAC model,[4] and the chemical part describes the conformational equilibria of sugars and the solvation equilibria between water and sugars. The physical part is described in terms of three new UNIFAC groups used to represent the sugar molecules: pyranose ring, furanose ring, and osidic bond that are

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