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Modeling of mixed-solvent electrolyte systems

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ABSTRACT: Models for mixed-solvent strong electrolytes, using an equation of state (EoS) are reviewed in this work. Through the example of ePPC-SAFT (that includes a Born term and ionic association), the meaning and the effect of each contribution to the solvation energy and the mean ionic activity coefficient are investigated. The importance of the dielectric constant is critically reviewed, with a focus on the use of a salt-concentration dependent function. The parameterization is performed using two adjustable parameters for each ion: a minimum approach distance (σ_{MSA}) and an association energy (ε^{AB}). These two parameters are optimized by fitting experimental activity coefficient and liquid density data, for all alkali halide salts simultaneously, in the range 298K to 423K. The model is subsequently tested on a large number of available experimental data, including salting out of Methane/Ethane/CO_2/H_2S. In all cases the deviations in bubble pressures were below 20% AADP. Predictions of vapor-liquid equilibrium of mixed solvent electrolyte systems containing methanol, ethanol are also made where deviations in bubble pressures were found to be below 10% (AADP).

Keywords: electrolytes, mixed solvents, dielectric constant, ePPC-SAFT, salting-out.

1. Introduction

The biorefining industry involves the conversion of biomass or organic material into fuel grade bio-diesel or bio-gasoline. The pre-treated biomass (feeding bio-refinery units) is a complex mixture of oxygenated hydrocarbons and water, a strongly polar solvent which forms a non-ideal mixture with the oxygenated chemicals. Water is also responsible for the degradation of processing equipment and worsening of product quality, so it needs to be separated. Aqueous solutions of salts have shown promising trend to aid in separation of these complex and oxygenated molecules encountered during the production processes of biofuel. The presence of an electrolyte causes a significant change in the equilibrium composition (especially liquid-liquid equilibrium), by altering the hydrogen bonding structure and other intermolecular forces. Hence, due to the addition of salt, the mutual solubilities change in either phase (aqueous phase and organic-rich phase). This behaviour is called the salting-out effect when the solubility decreases, and the salting-in effect when the solubility increases when adding salts [1,2]. This phenomenon is used in various industries (such as biorefining, pharmaceuticals or water treatment) for the separation of organic compounds. The use of electrolytes is however not limited to separation applications. They are often of interest in water treatment [3], geological, biological and