

# THERMODYNAMIC MODELING OF MIXTURES WITH MIXED SOLVENT ILS/SCCO<sub>2</sub> BY GROUP CONTRIBUTION

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## Abstract

In the past five years numerous applications using supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and ionic liquids (ILs) as mixed solvents have been published. One of the most important is the use as reacting media, taking the advantage of high solvent capacity of ILs plus the favorable transport properties of scCO<sub>2</sub>. Moreover, scCO<sub>2</sub> can be later used as extracting agent for products and unconverted reactants. Numerous chemical reactions have been performed in ILs, including hydrogenations, hydroformylations, Friedel-Crafts alkylation, Diels-Alder reactions and dimerizations. The systems organic substrates+ILs+scCO<sub>2</sub> present a complex phase behavior, which in general controls the outcome of processes using these mixed solvents.

ILs physical-chemical properties depend on the alkyl chain length, on the cation and the anion. Thus ILs can be designed to satisfy specific application requirements by properly choosing different negatively charged anions and positively charged cations with a number of alkyl structures. By combining various kinds of cation and anion structures, it is estimated that billions of ILs can be designed<sup>1</sup>. This fact suggests the convenience of using a group contribution approach to tailor mixed solvents ILs/scCO<sub>2</sub>.

Breure et al.<sup>2</sup> already showed the good capability of the Group Contribution Equation of State (GC-EoS)<sup>3</sup> to describe phase equilibria of systems containing scCO<sub>2</sub> and ionic liquids at high pressure. They extended GC-EoS to predict high-pressure phase equilibria in binary mixtures of CO<sub>2</sub> with the ionic liquids [-mim][PF<sub>6</sub>] and [-mim][BF<sub>4</sub>].

In this work we extend the GC-EoS to mixtures containing also organic substrates, besides the mixed solvents. The final goal is to obtain a thermodynamic model with good predictive capacity up to high pressures for designing mixed solvents taking advantage of the unique properties of both scCO<sub>2</sub> and ILs.

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