The Global Phase Diagram of Methane + Carbon Dioxide + Water from the SAFT-VR Approach

Jose Manuel Miguez
Universidade de Vigo, Departamento de Fisica Aplicada, Vigo, Spain

Maria Carolina dos Ramos
Vanderbilt University, Department of Chemical and Biomolecular Engineering, Nashville, TN, U.S.A.

Manuel M. Piñeiro
Universidade de Vigo, Departamento de Fisica Aplicada, Vigo, Spain

Felipe J. Blas [C, S]
Universidad de Huelva, Departamento de Fisica Aplicada, Huelva, Spain
felipe@uhu.es

Natural gas extraction from non conventional sources is gaining a remarkable relevance due to the increasing global demand of gas supply. These alternative sources include gas hydrates, coalbed methane, shale gas, and the tight-gas reservoirs (TGRs). Among them, TGRs are low permeability reservoirs and the extraction method commonly employed is the injection of an external aqueous based fluid, with the aim to modify the natural gas adsorption on the solid substrate, enhancing fluid recovery. Thus, the preliminary study of thermodynamic properties for bulk multicomponent mixtures that include methane, water, and other polar compounds plays a central role in this context. In this work, the molecular based Variable Range Statistical Associating Fluid Theory (SAFT-VR EOS) has been used to estimate the global phase equilibria diagram of the ternary mixture water + carbon dioxide + methane, over the whole composition range, and in pressure and temperature ranges close to those that are supposed to exist in TGRs. The CO_2 molecule is modeled as two spherical segments tangentially bonded, CH_4 as a spherical segment, and H_2O as a spherical segment with four associating sites to represent hydrogen bonding. A previous study on the phase behavior of the binary mixtures involved is also presented. The ternary mixture presents a very rich and complex phase behavior, with a wide region of the thermodynamic space of phases (at higher pressures) presenting a large gap of ternary liquid liquid equilibria, that upon descending pressures leads to the transition to a three-phase liquid-liquid-vapor equilibria region, and both regions are separated by a continuous critical end point line. The ability of the theory to describe this complex multicomponent mixture phase transition with a reduced and physically sound set of characteristic parameters must be underlined, as the parameters used to describe the involved binary mixtures were used in a transferable manner to estimate ternary phase equilibria without any further additional parameter.