Phase Equilibria and Interfacial Properties of Tetrahydrofuran + Carbon Dioxide Binary Mixtures from Experiments, Simulation, and Theory

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Tetrahydrofuran (THF) is a cyclic ether used as a thermodynamic hydrate promoter (THP) that produces a pronounced shift in the hydrate coexistence curves when used as an additive. Different authors have used THF for applications such as the reduction of the equilibrium pressure of hydrates of carbon dioxide (CO_2) for environmental concerns related with greenhouse gas emission control and effects on global climate change. In this work, we investigate the ability of different models of THF, when is mixed with CO2, in predicting phase equilibria and interfacial properties before using them for determining the equilibrium and structural properties of CO₂ hydrates with THF. This work focuses on the description of the interfacial behavior of this mixture at several temperatures and pressures, and can be considered as a preliminary study to predict the phase equilibrium of THF hydrates and hydrates of mixtures of THF with carbon dioxide. We consider three alternative but complementary approaches to characterize the interfacial properties of the system: experiments, molecular dynamics simulations, and theory. We determine interfacial tension, coexisting densities, concentration profiles along the interfacial region, surface activities, and relative Gibbs adsorption isotherms for the mixture at several vapor-liquid equilibrium conditions. Measurements are based on the use of a high-pressure pendant drop tensiometer coupled to a high-pressure densimeter. Theoretical modelling is carried out coupling the sophisticated SAFT-VR Mie equation of state with the Square Gradient Theory. Finally, molecular dynamics simulations are performed in the NVT canonical ensemble. We use two different united-atom models for THF, one flexible and another rigid. In addition to that, we also propose new coarse-grained molecular models for THF based on the SAFT-g Mie, also used in the theoretical description of the system. Theoretical models and computer simulation results indicate that CO2 accumulates at the liquid interface of tetrahydrofuran. Agreement between theoretical modelling and experiment is compared and analyzed in this contribution.