Advancements in Phase Equilibria Predictions and Modeling of Gas Hydrates

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Reliable gas hydrate phase behavior predictions are critical to petroleum and natural gas processing and other gas processing equipment. Inaccurate predictions of gas hydrate phase equilibria can also lead to erroneous design of process facilities, which may lead to safety hazards and flow assurance issues, including plugging of flowlines. The most significant advancement of gas hydrate phase equilibrium predictions is based on the statistical thermodynamic approach, introduced by van der Waals and Platteeuw (vdWP) in 1959. Over the next several decades the vdWP model was extended to model gas hydrate formation in multicomponent mixtures. In addition, some of the simplifying constraints in the original model, such as accounting for multiple guest occupancy and guest–guest interactions, were dropped. Surprisingly, little attention was given to correct the fluid phase part of the model. For instance, limitations in the fluid phase models include not accounting for the effect of molecules showing hydrogen bonding and also electrolyte contributions, which may lead to significant errors in most of the gas hydrate forming systems containing polar hydrate formers, inhibitors, and salts. Predictions of gas hydrate phase equilibria for polar hydrate formers and inhibited systems in presence of salts like NaCl, KCl, CaCl2, and also methanol, ethanol, monoethylene glycol, are critically important to flow assurance and operation. Unfortunately, the currently in use models show large errors in the fluid phase equilibrium predictions and since these models are inherently connected to the gas hydrate model, the overall gas hydrate phase equilibrium predictions are negatively affected. In particular, this is the case due to the following limitations: (1) the availability of vapor-liquid equilibria data for high salt concentrations, (2) appropriate electrolyte models (3) an equation of state accounting for association. To overcome these limitations, this work reviews and implements various fluid phase equilibrium models for improved predictive capabilities for a range of hydrocarbons, from low to higher molecular weight, polar components, organic inhibitors and electrolytes.