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Thermodynamic prediction of clathrate hydrate dissociation conditions in mesoporous media

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ABSTRACT

We present modifications to a previously reported statistical thermodynamics model that facilitates the prediction of capillary pressure effects on hydrate equilibria in narrow pores. The model uses the Valderrama modification of the Patel and Teja Equation of State (VPT EoS) for fugacity calculations in fluid phases, while the hydrate phase is modeled using the solid solution theory of van der Waals and Platteeuw (1959), as implemented by Cole and Goodwin (1990). The Kihara model for spherical molecules is applied to calculate the potential function for hydrate-forming gases. To account for capillary pressure effects on phase fugacities, we apply a correction similar to the Poynting correction for saturated liquids. This correction can be applied to any model capable of predicting bulk (unconfined) hydrate phase equilibria. The only new parameter required is hydrate-liquid interfacial tension—values for which we have derived previously from experimental data. The model assumes cylindrical pores, although differs from the majority of existing literature models in how the curvature of the solid-liquid interface is considered; we assume a curvature of $2/r$ for growth and $1/r$ for dissociation, in accordance with accepted capillary theory. Model predictions are validated against previously published experimental hydrate dissociation data for binary CO_2-H_2O, CH_4-H_2O and ternary CH_4-CO_2-H_2O systems, and newly reported data for CH_4-H_2O-CH_4O (3.5 mass% methanol aqueous solutions representing the salinity of seawater) systems, confined to mesoporous silica glass. Good agreement between predictions and experimental data is observed.