Modeling Gas Hydrate Phase Equilibria in Laboratory and Natural Porous Media

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A method to predict hydrate phase behavior in laboratory-prepared and natural porous media is presented. This model extends both the van der Waals and Platteeuw (vdWP) approach and our fugacity-based approach to porous media by accounting for the effects of both surface energy and pore size distribution. Our fugacity approach quantitatively predicts the equilibrium pressure–temperature relation for hydrates in laboratory porous media above the normal freezing point of water without any empirical corrections to the surface contact parameters, as have previously been required with the vdWP model. A pore size distribution model that depends on the soil type and pressure is developed and then used to predict methane hydrate formation in natural porous environments. The maximum depth of ocean hydrates using our fugacity-based model with the pore size correction is calculated for seven drilling sites. Our predictions for the hydrate depth have an average deviation of 4.9% compared to the experimental data, which is less than the 11.6% AAD using the common approach of assuming that the phase behavior in the pores is identical to that in the bulk.

Introduction

Gas hydrates or clathrates are crystalline compounds that form from water with at least one other compound, and they can form at conditions above the normal freezing point of water. The crystalline lattice forms a network of cages that trap guests necessary for the stability of the lattice. Various types of guests are known to form hydrates, but the ones of main interest here are methane and propane, which are hydrophobic and ubiquitous in the environment. These guests are of particular interest in the petroleum industry, as well as to geologists and environmentalists. Large masses of hydrates exist in the deep ocean floors and permafrost regions, and hydrates can form in natural gas pipelines where they can obstruct flow.

Hydrate structures I and II are of main interest here. Structure I (sI) is a body-centered cubic structure with a lattice parameter of 12.03 Å and with ethylene oxide as the guest. The cubic cell contains 46 H2O molecules, 2 12-hedra (512), and 6 large voids (51262), where 512 is used to indicate that the polyhedra contain 12 five-membered-ring faces and the 51262 cell also contains 2 six-membered rings. Structure II (sII) is a body-centered cubic structure with a lattice parameter of 17.31 Å for a double hydrate with tetrahydrofuran and hydrogen sulfide as guests. Each cubic cell contains 136 water molecules, 8 large voids (51264), and 16 12-hedra. The lattice constant depends on the guest as the guests vary in size, shape, and chemical functionality and therefore distort the lattice differently.3,4

There is interest in developing methods to harvest the huge amounts of methane present in natural gas hydrates. A recent estimate of the amount of methane trapped in hydrates is as much as 300 times that in conventional U.S. reserves.5 Also, the melting and dissociation of gas hydrates in the ocean floor and in permafrost regions might increase global warming.6,7 resulting in further hydrate dissociation. Conversely, sequestering of carbon dioxide in hydrates has been proposed to reduce the amount of this greenhouse gas in the environment. Brewer et al.8,9 have experimentally shown growth of CO2 hydrates in the ocean, which might lead to a method for CO2 removal from the atmosphere.

Most measurements and models have been of bulk gas hydrates, which is important in pipelines. However, hydrates in nature largely occur in porous media, e.g., clay, silt, and sand. Because capillary forces become important in porous media, the hydrate equilibrium pressure increases as the pore size decreases. Handa and Stupin10 first studied the effect of the porous media on equilibrium pressures of methane and propane hydrates. Uchida et al.11 measured the equilibrium pressures for methane hydrates in pores of different sizes.

Recently, Clarke et al.12 developed a method for predicting hydrate phase behavior in submicron-sized pores. They added a term to the bulk hydrate model developed by van der Waals and Platteeuw13 (vdWP) to include the effect of surface tension. Clarke et al.12 assumed that the porous media in the work by Handa and Stupin12 consisted of pores of a single size rather than a distribution of sizes. The model we present here includes the experimentally known distribution of pore sizes in the vdWP model and in the fugacity-based model recently developed by us.14

Hydrate Formation in Porous Media

Recent papers15,16 describe the formation of hydrates in the sediments of the ocean and in permafrost regions. The capillary forces between the solid phase and liquid water in the pores of sand or other sediments raises the equilibrium pressures above that of the bulk phase.10 Natural porous media, e.g., sand and silt, have varying

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