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Theoretical modeling of the gas hydrates of nitrous oxide and methane mixtures

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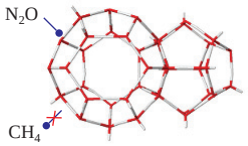
Thermodynamic conditions for the formation of the clathrate hydrates of N_2O + CH_4 gas mixtures have been determined by computer simulation with special emphasis on the possibility of using hydrates for the storage of greenhouse gases.



Gas hydrates are the nonstoichiometric solid compounds of gases and water. They are of importance with respect to safety issues in oil and gas pipelines, energy recovery and transportation, and past and future climate changes.[1] Greenhouse gas control is topical for the solution of environmental problems. The most common greenhouse gases are methane, carbon dioxide, tetrafluoromethane and nitrous oxide. Materials based on the clathrate hydrates of greenhouse gases make it possible to reduce the volume of gases by a factor of several hundreds. The results of experimental and theoretical studies on the stability and composition of gas hydrates have been published.[1–11] However, only very limited data on formation–dissociation conditions are available for the hydrate of nitrous oxide.[12–14] The stability of nitrous oxide clathrate hydrates in a temperature range from 266.7 to 285.1 K and at pressures from 0.74 to 4.13 MPa has been estimated[12] and experimental data on nitrous oxide hydrate dissociation have been obtained.[13]

The aim of this work was to study the effect of methane on the phase behavior of nitrous oxide gas hydrate systems. We determined the conditions of formation and the temperature and pressure dependences of the composition of gas hydrates formed from nitrous oxide and methane gas mixtures. The thermodynamic model used was described in detail previously.[15] The unit cells of CS-I and CS-II hydrates[1] were chosen as simulation cells. It was expected that large and small cages to be filled by one N_2O or CH_4 molecule. The double filling of large or small cages by these guest molecules was not considered due to a comparatively large size of these molecules. For the modeling of ice I_h, a simulation supercell containing 32 unit cells, *i.e.*, 128 water molecules, was used. Coulomb interactions were calculated by the Ewald method with an arrangement of hydrogen atoms satisfying the ice rule.[16] Interactions between water molecules in hydrates and ice were described by the modified SPC/E potential.[17] The choice of parameters allows one to reach good agreement with experimental data.[18,19] For the description of interactions of guest molecules between each other and with water molecules, the simple Lennard–Jones potential for spherical particles was used with parameters published for methane[20] and nitrous oxide[21] molecules.

The thermodynamic properties of crystals and the guest inclusion behavior of nitrous oxide hydrates with and without methane were studied using the previously developed approach[15] based on a combination of molecular dynamics, lattice dynamics and statistical thermodynamic methods. At first, the equilibrium positions of water and guest molecules were calculated using molecular dynamics simulation at $T = 0$ K. It is necessary because the intermolecular potential chosen for modeling can influence the crystal geometry. At the next step, the lattice dynamics was used to calculate potential energy, full spectrum of lattice vibrations and Helmholtz free energy as functions of the temperature and volume of modeling cell. Due to periodic boundary conditions, the intermolecular interactions include interactions with the molecules of neighboring simulation cells. This excludes the influence of boundaries on the state of the simulation cell. The data obtained allow one to calculate consequentially the equation of state and Gibbs free energy for a given hydrate phase and then to determine the filling of cages in dependence on pressure and, finally, the chemical potentials of water molecules in hydrates. A similar approach was applied to calculate the chemical potential of water molecules in ice. For determining the chemical potential of water molecules in a liquid phase, an empirical approach[22] was used. The points on phase diagrams were found as the intersection points of chemical potentials for ice (water) and hydrate in dependence on pressure at a given temperature.

Thermodynamic calculations have demonstrated that a pure N_2O hydrate has structure I (CS-I), and N_2O–CH_4 mixed hydrates have structure I. For the pure N_2O hydrate, the degrees of filling of small and large cages were calculated. The occupancies of small and large cages of CS-I hydrate by N_2O molecules at $T = 270$ K and $P = 0.1$ MPa were estimated at 0.82 and 0.98, respectively. The phase equilibrium conditions of pure N_2O and binary N_2O–CH_4 hydrates were determined and compared with experimental data (Figure 1). Our model allows us to predict the phase stability

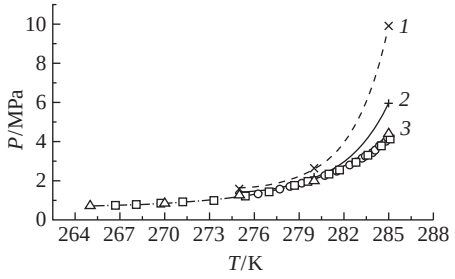


Figure 1 Pressure *vs.* temperature diagram: (*1*) binary hydrate of N_2O and 25% CH_4 in a gas phase, (*2*) binary hydrate of N_2O and 10% CH_4 in a gas phase, and (*3*) pure hydrate of N_2O; (□) and (○) are the data for $N_2O \cdot H_2O$ from refs. 12 and 13, respectively.

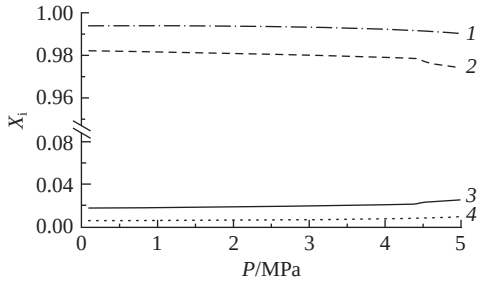


Figure 2 Mole fractions of N_2O and CH_4 *vs.* pressure in the large and small hydrate cages of a binary hydrate at T = 270 K. Gas phase contains 10% and 25% CH_4. Fraction of N_2O with (*1*) 25% and (*2*) 10% CH_4 in a gas phase; fraction of CH_4 with (*3*) 25% and (*4*) 10% CH_4 in a gas phase.

boundary and cage occupancies for the pure N_2O hydrate, which are consistent with published experimental results.[12–14]

The three-phase coexistence curves for N_2O hydrate–liquid water–N_2O gas and N_2O hydrate–Ice I_h–N_2O gas were determined up to 6 MPa using the previously developed approach.[15] Analogous calculations for binary $N_2O + CH_4$ hydrates have been performed for pressures up to 10 MPa within the same approach.

Methane has a significant effect on the three-phase equilibrium curve in the test region of pressures and temperatures. Thus, on the addition of only 25% CH_4 to the gas phase, the hydrate formation pressure for pure N_2O at 285 K increased from 4.4 to almost 10 MPa. At lower temperatures, changes in the hydrate formation pressure were not so notable.

The stability of N_2O clathrate hydrates CS-I at 0.707–4.4 MPa and 265–285 K was demonstrated. Figure 2 shows the mole fractions of N_2O and CH_4 as functions of pressure up to 5 MPa at T = 270 K. An increase in the pressure leads to a very slow increase in the methane content of the hydrate. Even at 25% CH_4 in the gas phase, its mole fraction in the hydrate was lower than 3%. Thus, the hydrate formation pressure can be lowered in order to develop a method for the separation of gases using clathrate hydrates.

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