Thermodynamic properties of propane and methane hydrates doped with sodium hydroxide

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Abstract. Pure and sodium hydroxide doped with single-component hydrates of methane and propane are studied using molecular and lattice dynamics methods. Vibration density of states and the dependence of Helmholtz free energy on temperature and cell volume are calculated. Dynamic stability of empty and filled by gas sI and sII structures is shown in the wide range of temperature values. Comparison of free energy values allows calculating the thermal expansion coefficient and demonstrating the possibility of self-preservation effect in NaOH-doped methane and propane hydrates with ~1.8 and ~1.4 mol% of sodium hydroxide, respectively.

1. Introduction
The possibilities of using clathrate hydrates [1] are wide: storage and transportation of natural gas, disposal of greenhouse gases, hydrogen extraction from synthesis gas (syngas) and its use in green energy. As inclusion compounds, clathrate hydrates can contain gas and light liquids (guests) in their cavities formed by a H$_2$O framework (host), interacting with water due to van der Waals forces. An important advantage is the ability to form hydrates of some compounds at T > 0°C and their thermodynamic stability.

Hydrates of some gases can also persist at atmospheric pressure and T < 0°C, when an anomalously low rate of hydrate decomposition is observed [2–4]. The so-called self-preservation effect is manifested due to the formation of ice layer on hydrate surface. This layer may have lower thermal expansion coefficient than the hydrate has, that leads to excess pressure creation during the heating [5] and, consequently, the maintenance of the hydrate stability conditions. However, not all guests can reveal the self-preservation effect [6, 7].

Doping may significantly enhance thermodynamic, selective or other properties of hydrates. Doped hydrates differ from ionic clathrate hydrates [8] in their low impurity fraction, however in both cases additives interact with water framework via stronger forces. As a result, hydrophilic cations fill the cavities or hydrophilic anions are incorporated into host lattice. For example, potassium hydroxide (KOH) doping (~0.1 mol%) could increase the hydrate melting point [9]. Tetrahydrofuran (THF) doping significantly reduces the induction time, increases the methane uptake rate, lowers the formation pressure and increases the melting point [10, 11] with ~5.6 mol% concentration of THF. Also, KOH-doping of THF hydrate solution drastically increases the dynamics of protons (H$^+$ in H$_2$O) and leads to the ordering of protons at ~72 K and ~0.19 mol% of KOH [12].

The search for new additives is an important task, and its results may assist in lowering the hydrate formation pressure, increasing the hydrate melting point or improving the hydrate formation kinetics.
or selectivity in gas separation. The proposal to use sodium hydroxide for these purposes can be dictated by the fact that the melting point of NaOH–nH2O hydrates is higher when n is lower [13]. However, NaOH-doped hydrates themselves have not yet been studied much. Sodium hydroxide is used to neutralize acidity of CO2 gas from natural gas and to increase the methane concentration before the hydrate formation [14] or as a part of electrolyte solution for methane hydrate formation [15].

The aim of this work is to study the dynamic and thermodynamic properties of methane and propane hydrates in the 100 – 280 K temperature range using the quasi-harmonic lattice dynamics method and to investigate the influence of doping hydrates with sodium hydroxide on vibration density of states, Helmholtz free energy and thermal expansion coefficient. Another important task is to study the possibility of self-preservation effect in NaOH-doped hydrates of propane and methane.

2. Methods

Similar to our previous work [16], the non-doped and doped with 1 or 2 NaOH molecules hydrate cubic structures I (sI) and II (sII) were considered. Non-doped structures were represented as single unit cells containing 46 (sI) and 136 (sII) water molecules: 2·512+6·51262 and 16·512+8·51264 small and large cavities, correspondingly. Doped structures were obtained by the replace of 1 or 2 water molecules by sodium hydroxide molecules in such a way as to keep one hydrogen bond and orient the HO−Na+ bonds into the empty cavity. To match the experimental data, only 7 cavities of sI were filled with methane and only large (8) cavities of sII were filled with propane. Periodic boundary conditions were set to avoid the effects of system size finiteness.

The intermolecular interactions were described by Coulomb electrostatic (used Ewald summation: real-space cut-off range of 13 Å and 10–8 relative accuracy) and van der Waals (6-12 Lennard-Jones potential) interactions. Water molecules were described by the modified SPC/E mod potential. Methane and propane molecules were described in single-particle approach. Water molecules and hydroxyl groups were considered as rigid. SPC/E mod Lennard-Jones potential parameters used for H2O oxygen atoms were \( \sigma = 3.1556 \text{ Å} \), \( \varepsilon = 0.65063 \text{ kJ/mol} \) and charges were \( q_{O} = -0.8476 |e| \), \( q_{H} = +0.4238 |e| \) [17], non-charged CH4 particle parameters were \( \sigma_{CH4} = 3.73 \text{ Å} \), \( \varepsilon_{CH4} = 1.2305 \text{ kJ/mol} \) [18], non-charged C3H8 particle parameters were \( \sigma_{C3H8} = 5.637 \text{ Å} \), \( \varepsilon_{C3H8} = 2.013 \text{ kJ/mol} \) [19], OH− oxygen atoms parameters were \( \sigma_{OH} = 3.12 \text{ Å} \), \( \varepsilon_{OH} = 0.71094 \text{ kJ/mol} \) and charges were \( q_{OH} = -1.418 |e| \), \( q_{NaOH} = +0.418 |e| \) [20], Na+ atom parameters were \( \sigma_{Na} = 2.117 \text{ Å} \), \( \varepsilon_{Na} = 1.973 \text{ kJ/mol} \) and charge \( q_{Na} = +1 |e| \) [21], where \( e \) was the electron charge. Standard mixing rules for Lennard-Jones parameters were used.

Structure optimization was conducted using the gradient descent algorithm. Thermal expansion coefficient was calculated from equation of state using data on Helmholtz free energy of the system obtained from the quasi-harmonic lattice dynamics method and calculated vibration spectrum. Details may be found in [17]. This method has shown an excellent agreement with experimental phase diagrams and thermal expansion coefficients of amorphous ices and gas hydrates [22-25]. The study was conducted in 100 – 280 K temperature range. Hexagonal ice (Ih) structure, that was used to check the self-preservation effect possibility, contained 512 water molecules.

3. Results

Vibrational densities of states (VDoS) of non-doped and doped empty and filled hydrate structures are presented in Fig. 1. Dynamic stability of considered structures is shown by the absence of frequencies with complex values of dynamic matrices calculated in this work, that means all molecules are in potential energy minima. Usually, vibration spectrum of water-based crystals is low-frequency translation and high-frequency rotation vibration region, and the gap between them is in the ~300 – ~500 cm\(^{-1}\) region. It can be seen that NaOH doping is revealed as new sharp peaks in the gap region and in the ~1200 – ~1300 cm\(^{-1}\) region. The effect of sodium hydroxide on water and gas vibrations is sufficient in the case of sI structure only. Due to lower molar concentration in sII structure the effect of NaOH on VDoS is less pronounced. In the same way as for KOH doping [16], the increase of NaOH concentration leads to the “blur” of methane vibration peak (~25 cm\(^{-1}\)) as well as lowering and
broadening of ~150 – 300 cm\(^{-1}\) translation vibration part of sI VDoS. Peaks in ~1200 – ~1300 cm\(^{-1}\) region appear due to the incorporation of OH\(^-\) group into the water framework and shifting of Na\(^+\) ions towards the cavity hexagon face that causes local potential redistribution for H\(_2\)O molecules. Na\(^+\) ions themselves have low-frequency translation vibrations and merge with H\(_2\)O peaks.

**Figure 1.** VDoS of NaOH-doped and non-doped (top left) empty sI framework, (top right) empty sII framework, (bottom left) methane hydrate and (bottom right) propane hydrate.

Using the vibration data, the Helmholtz free energy normalized on H\(_2\)O molecule number was calculated for 100 – 280 K temperature range with 10 K step for every cell volume obtained after optimization of compression and decompression (quasi-harmonic approximation) process. Resulting dependences for non-doped and doped structures are presented for \(T = 200, 250, 270\) and 275 K in Fig. 2. Filling of cavities by methane or propane leads to Helmholtz energy decrease. Every NaOH molecule doped into a hydrate structure leads to free energy decrease by 20 kJ/mol (sI) and 6.5 kJ/mol (sII). The difference between these numbers corresponds to the ratio of unit cell water molecule number. Comparison of non-doped and doped structures shows the increase of absolute values with sodium hydroxide concentration increase for both sI and sII structures with filled and empty cages. This may indicate the energetic advantage of the formation of NaOH-doped hydrates, however the chemical potential calculation and taking entropy contribution into account are necessary to study the thermodynamic stability and structure preferences.
Figure 2. Helmholtz free energy normalized on water molecule number dependence on unit cell volume for non-doped, doped with 1 or 2 NaOH molecules empty sI and sII frameworks, methane and propane hydrates at 200, 250, 270 and 275 K.

Figure 3. Comparison of thermal expansion coefficient of non-doped and NaOH methane and propane hydrates with Ih ice.

Helmholtz free energy dependences minima presented in Fig. 2 correspond to the zero-pressure volume at a given temperature, while negative and positive slopes correspond to the volumes of unit cells under positive and negative pressure, respectively. Thermal expansion coefficient data in comparison with Ih ice data is presented in Fig. 3. Non-doped methane hydrate has higher thermal expansion coefficient and slope compared to ice, that indicates the self-preservation effect possibility, while non-doped propane hydrate has close value and slope of thermal expansion coefficient making self-preservation unlikely. These results correspond to experimental data f [6]. New results open the way to search for the possibility of self-preservation of CH₄ hydrate doped by 1 NaOH molecule.
(~1.8 mol%) and C$_3$H$_8$ hydrate doped by 2 NaOH molecules (~1.4 mol%). Methane hydrate doped by 2 NaOH molecules (~3.6 mol%) and propane hydrate doped by 1 NaOH molecule (~0.7 mol%).

**Conclusions**

Using quasi-harmonic lattice dynamics approach, the dynamic stability of sodium hydroxide-doped hydrates of methane and propane has been shown. The NaOH additive has an effect in the lowest frequency region, the gap region and the [~1200; ~1300] cm$^{-1}$ region, that corresponds to the translation vibrations on Na$^+$ ions, OH$^-$ group and violation of crystal lattice geometry due to doping, correspondingly, for both methane/propane hydrate. Spectrum peaks in the 1200 – 1300 cm$^{-1}$ region can be an indicator of NaOH presence in experimental studies. NaOH concentration increase leads to gain of shift of water translation vibrations in methane hydrate.

For the considered molar fractions of the additive, sodium hydroxide molecules are found to linearly affect the Helmholtz free energy at comparable values for methane and propane hydrates, taking into account the NaOH molar fraction.

Calculation of thermal expansion coefficients of I$_h$ ice, methane and propane hydrates have shown the possibility of self-preservation effect for methane hydrate doped with 1 sodium hydroxide molecule per unit cell and for propane hydrate doped with 2 sodium hydroxide molecules.

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