Thermodynamic properties of methane and propane hydrates doped by potassium hydroxide

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Abstract. Using conjugate gradient and lattice dynamics methods the theoretical study of thermodynamics properties of methane sI and propane sII hydrates doped with small amount of potassium hydroxide was conducted. Potassium hydroxide was partially embedded in the host framework lattice of hydrate. The vibration densities of states were found and the stability of the doped hydrate was confirmed. For a wide range of temperatures the free energy curves were built and compared to results for non-doped hydrate structures. Based on this data the thermal expansion coefficient dependence on the temperature was calculated and the possibility of methane and propane hydrate self-preservation was studied.

1. Introduction

Classical clathrate hydrates are inclusion compounds that confine non-ionic compounds in the cavities of the hydrogen bonded water framework. At certain conditions hydrates are thermodynamically more stable than ice or water. In gas hydrates, the guest molecules interact with the host water molecules only through the Van der Waals forces. In contrast, ionic clathrate hydrates (ICH) form many clathrate structures with the inclusion of hydrophobic cations into the cavities, or the embedding of hydrophilic anions of relatively small size in the water framework itself, or a simultaneous inclusion of hydrophilic and hydrophobic components of multiatomic compounds [1]. The compounds included in the ICH structure form stronger chemical bonds with the host lattice.

The structure of monohydrate KOH·H₂O has been known for a long time [2], the melting temperature being 400 K [3]. Later the other KOH·nH₂O compounds were discovered, where n = 2, 4 and 5. Dihydrate (n = 2) melts at ~306 K, tetrahydrate (n = 4) decomposes at ~239.5 K, and the most water-saturated pentahydrate (n = 5) melts at ~207.5 K with decomposition into tetrahydrate and ice [4]. At low temperature the doping of KOH leads to a significant increase in the proton dynamics of the aqueous framework and establishes proton ordering at lower temperatures with tetrahydrofuran clathrate hydrate [5, 6]. In these works, the KOH mole fraction was chosen to be 10⁻³–10⁻⁴ in comparison with water. Much more significant addition of KOH (~0.1 from water mole fraction) in the initial aqueous solution leads to an increase in the melting point of the ICG [7]. The authors of this paper suggested that K⁺ may be located in a cavity, while OH⁻ is embedded in host lattice.

One of the unique properties of hydrates is the effect of self-preservation – abnormally low decomposition rate at atmospheric pressure and at temperatures below 0º C, but outside the thermobaric stability region [8]. Unfortunately, not all gas hydrates show this dissociation anomaly [9].
The importance of studying gas hydrates is related to the development of natural gas storage and transportation technologies: almost 25% of savings in gas transportation in the form of hydrates were shown in comparison with liquefied natural gas transportation. [10]. One of the important tasks in this case is to increase the melting point of gas hydrates.

In this work the theoretical study of the thermodynamic properties of methane sI hydrate and propane sII hydrate doped with potassium hydroxide is conducted. The conjugate gradients method and the lattice dynamics method are used. The aim of the work is to study the influence of potassium hydroxide on the vibrational spectrum of hydrates, to determine its contribution to the free Helmholtz energy and to study the possibility of self-preservation effect in KOH-doped methane and propane hydrates.

2. Methods

The calculations performed in this paper are based on thermodynamic modelling of methane and propane hydrate structures. The cubic unit cell of sI hydrate (cell size is 12.0 Å) containing 46 water molecules and the cubic unit cell of sII hydrate (cell size of 17.1 Å) containing 136 water molecules were taken to model empty structures as well as the methane and propane hydrates. Structure sI contains two 512 cavities and six 51262 cavities whereas sII contains eight 51264 cavities and sixteen 512 cavities. According to experimental data, only seven sI cavities were occupied by methane molecules and only 51264 sII cavities were occupied by propane molecules. The structures of doped hydrates were constructed by replacing one water molecule placed in the apex of the polyhedron of the empty cavity, with a potassium hydroxide molecule so that the oxygen position remains the same, and the potassium hydroxide’ O-K bond is directed inside the empty cavity. In this case, one of the hydrogen bonds that existed for the removed water molecule is retained and potassium atom is inside the cavity. Gas molecules were considered in one-particle approximation. Periodic boundary conditions were applied. The study was conducted in the temperature range from 230 to 280 K.

The method of conjugate gradients was used to find optimal positions of all molecules, i.e. to find the minimum energy of each molecule. In the process of optimization, each molecule shifts in the direction of the forces applied to it in proportion to the value of these forces. Optimization by the method of conjugate gradients continues until the difference in total energy between the optimization steps and forces in the system become less than the selected criterion. The interaction between the molecules was calculated as a sum of electrostatic and van der Waals interactions, which in turn was described using the Lennard Jones potential. The potential energy $U(r)$ between particles $i$ and $j$ is presented in the form:

$$U_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] - \frac{q_i q_j}{r}, \quad (1)$$

where $r$ is the distance between particles $i$ and $j$, $q$ is the particle charge, $\sigma_{ij}$ and $\varepsilon_{ij}$ are the distance and energetic constants of Lennard-Jones potential and could be defined with the following combination rules: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$. Modified SPC/E potential was used to describe water molecules and Lennard-Jones potential parameters were used only for oxygen atoms: $\sigma = 3.1556$ Å, $\varepsilon = 0.65063$ kJ/mol. Charges are presented for both types of atoms: $q_{OH} = +0.4238|e|$ for hydrogen atoms and $q_{O} = -0.8476|e|$ for oxygen atoms, where $e$ is the electron charge. The following Lennard-Jones parameters were set for methane particles $\sigma = 3.73$ Å and $\varepsilon = 1.2305$ kJ/mol; propane particles $\sigma = 5.637$ Å and $\varepsilon = 2.013$ kJ/mol; potassium atoms $\sigma = 2.791$ Å and $\varepsilon = 2.223$ kJ/mol [11]; oxygen in OH$^-$ $\sigma = 3.12$ Å and $\varepsilon = 0.71094$ kJ/mol [12]. The molecules of methane and propane were considered electrically neutral. Potassium hydroxide atom charges are $q_{K} = +1|e|$, $q_{O} = -1.418|e|$, $q_{H} = +0.418|e|$ [13]. The water and potassium hydroxide molecules were considered as rigid. The K–O distance in linear KOH molecule was set to 2.557 Å [14]. The water and potassium hydroxide molecules were considered as rigid.

The lattice dynamics (LD) method was used to calculate the molecular vibration frequencies. This
method uses quasi-harmonic approximation \cite{15} and allows calculating the vibrational spectrum, density of vibrational states and the vibration part $F_{\text{vib}}$ of Helmholtz free energy $F = U + F_{\text{vib}}$:

$$
F_{\text{vib}} = \frac{1}{2} \sum_{jq} \hbar \omega_j (\bar{q}) + k_B T \sum_{jq} \ln \left( 1 - \exp \left( \frac{-\hbar \omega_j (\bar{q})}{k_B T} \right) \right). \tag{2}
$$

The volumetric differentiation of the Helmholtz free energy allows determining the pressure in the system:

$$
P(V,T) = -\frac{\partial F(V,T)}{\partial V}. \tag{3}
$$

At pressure close to zero it is possible to determine the thermal expansion coefficient of gas hydrates. The procedure described above is similar to that in \cite{16} and is described in detail in \cite{17,18}.

3. Results

Fig. 1 shows the vibration density of states (VDOS) for the studied systems. The absence of negative frequency values usually means that all molecules are in the minimum potential energy and structures are dynamically stable. It can be seen that both non-doped and KOH-doped structures are dynamically stable. Pure water-based crystal structures including hydrate structures have $[0; 300]$ cm$^{-1}$ vibration region corresponding to translation molecular vibrations, $[500; 1000]$ cm$^{-1}$ vibration region corresponding to rotational vibrations and $[300; 500]$ cm$^{-1}$ region that corresponds to the gap between the regions of translation and rotational vibrations. Comparison of doped and non-doped structures filled and not filled with guest molecules shows that KOH molecules mainly contribute to the region $[300; 500]$ cm$^{-1}$ corresponding to the gap area and weakly affect other regions is the case of sII structure that could be due to the ratio between the number of KOH and H$_2$O molecules that also explains the difference of gap peak heights between sI and sII structures. Presence of KOH in sI structure leads to $\sim 15$ cm$^{-1}$ shift towards higher values of translation vibration region and smearing of methane peak (20–30 cm$^{-1}$). This indicates a strong interaction of potassium hydroxyde group with water molecules and methane and neglectable interaction with propane molecules.
Figure 1. VDOS of non-doped and KOH-doped sI and sII structures without guest molecules (empty) and with guest molecules.

The temperature range under study is relatively easy to reach at atmospheric pressure that opens up possibilities for wide applications. Fig. 2 presents the dependence of cell free energies on the model cell volume at temperature 250, 260, 270 and 275 K and shows the negative slope region, which according to the equation (3) corresponds to the positive pressure region. The lowest free energy value for each curve corresponds to zero pressure model volume. Comparison of Helmholtz free energies for the KOH-doped and non-doped structures describes the strong interaction between KOH and H2O molecules. Free energy absolute values are greater in the case of KOH-doped sI structure and non-doped sII structure. This may indicate the energy profitability of these structures, however, the calculation and comparison of water molecule chemical potentials is required for greater accuracy.
Figure 2. The dependence of model cell free energy on the volume of non-doped and KOH-doped sI and sII structures without guest molecules (empty) and with guest molecules at different temperatures.

The results presented in Fig. 2 allow determining the dependence of the structure volume on the temperature at zero pressure and calculating the relative coefficient of thermal expansion. Fig. 3 presents the relative thermal expansion coefficient for KOH-doped methane and propane hydrates and crystalline ice with hexagonal structure Ih [16]. It can be seen that the thermal expansion coefficient for doped methane hydrate is higher than for ice that may indicate the possibility of self-preservation phenomenon: upon hydrate melting an ice crust forms on its surface and can withstand the excess pressure of hydrate faster expanded when heated. This excess pressure transfers the gas hydrate to the region of thermodynamic stability and provides hydrate preservation.

Figure 3. Relative thermal expansion coefficient of KOH-doped hydrates and ice Ih [16] normalized to volume at 230 K.
Conclusions
Within the framework of the lattice dynamics method, the dynamic properties of sI methane and sII propane clathrate hydrates have been investigated and the dynamic stability of potassium hydroxide doped hydrates has been demonstrated. The peculiarities of the vibration density of states of doped hydrate structures, i.e. the influence of KOH on the water structure, found in the [300; 500] cm$^{-1}$ gap region, a shift of sI translation vibration frequencies towards higher values as well as the smearing of methane translation vibration peak, can be explained by the interaction of potassium hydroxide with water molecules. The contribution of potassium dioxide to the free energy on cell volume at different temperatures leads to 7-10% value shift in empty and filled hydrate structures. The relative thermal expansion of methane and propane hydrates doped with potassium hydroxide has been calculated to show that the expansion of doped methane hydrate grows faster than for crystal ice Ih. Based on this, it is concluded that self-preservation is possible for such compound.

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