Theoretical investigation of thermodynamic properties of tetrabutylammonium bromide ionic clathrate hydrate

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Abstract. In the framework of the lattice dynamics method, the densities of the phonon states of tetrabutylammonium bromide ionic clathrate hydrate have been found. The dynamic stability of the hydrate is shown for a number of temperatures. Using the developed statistical-thermodynamic theory, the free energy curves have been constructed for a wide range of temperatures at different unit cell volumes and, based on the calculated data, the lines of thermal expansion of the hydrate have been constructed.

1. Introduction

Inclusion compounds formed by water molecules and quaternary ammonium or phosphonium salts are representatives of a vast group of ionic clathrate hydrates (ICH) or semiclathrate hydrates, which structures were in detail investigated by Jeffrey [1]. Chloride and bromide of these salts are commonly used because of the stability of obtained structures and low toxicity of these salts. Unlike conventional clathrate hydrates, where guest molecules interact with host lattice by only van der Waals forces, salts incorporated in ICH structure form chemical bonds with water molecules [2]. ICH may contain guest molecules only at small dodecahedral cages, whereas other cages are occupied by butyl chains of cations and anions. However the presence of salts significantly reduces the pressure of hydrate formation [3,4] and the irregularity of the structure leads to an increased selectivity for the similar size molecules [5, 6]. Low cost of hydrate formation makes ICH a promising material for separation of flue and fuel gas mixtures, as well as for separating greenhouse carbon dioxide gas for its subsequent utilization [7]. Tetrabutylammonium bromide (TBAB, C\textsubscript{16}H\textsubscript{36}NBr) is a well known and widely used in different applications. It also known that it forms tetragonal and orthorhombic ICH structures [8].

In present paper we are presenting results of numerical calculations of phonon density of states, Helmholtz free energy at different temperatures and atmospheric pressures for one of modeling orthorhombic TBAB ICH structures.

2. Theoretical model and methods of simulations

2.1. Model of tetrabutylammonium bromide hydrate

In our simulation the only one initial structure of TBAB ICH was used. The structure contains 76 water molecules and two TBAB molecules. Organic salts TBAB molecules were positioned so that they compensated dipole moment each other as it shown on figure 1. The unit cell parameters for
chosen orthorhombic structure were varied in large intervals to find most stable structure, for example, cell vector $a$ varied from 21 Å to 23 Å. These parameters were changed for different temperatures from 230 K to 283 K.

Figure 1. Structure of modelled TBAB ICH. The oxygen and hydrogen atoms forming water molecules are shown by red and white sticks, the carbon, nitrogen and bromine atoms are represented by gray, blue and dark red spheres, respectively. The TBAB forming hydrogen atoms are represented by white sticks.

Figure 1 also demonstrates that bromine anions in the hydrate interpose in host lattice forming with surrounding water molecules hydrogen bonds.

2.2. Methods of simulations

The initial modeling structure can be non-optimal and molecules can be located out of their energy minima positions. Thus, first step of simulation consists of finding the structure with minimal energy for each molecule in a system. It was done within the framework of conjugated gradient method, in which molecules move every step in the direction of moving forces on the distance proportional to the force value. To calculate the force potential of intermolecular interactions the potential energy was calculated as sum of van-der-Waals interactions and electrostatic interactions in a form:

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

(1)

There $U_{ij}(r)$ is the potential energy between i an j atoms; $\sigma_{ij}$ and $\varepsilon_{ij}$ are determined from combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j}$. Lennard-Jones parameters of water molecules are used only for oxygen atoms: $\sigma = 3.1556$ Å and $\varepsilon = 0.65063$ kJ/mol. Charges are presented on both atoms: $q_H = +0.4238$ |e| for hydrogen atoms and $q_O = -0.8476$ |e| for oxygen atoms. Lennard-Jones parameters for TBAB molecule were chosen as follows: for nitrogen $\sigma = 3.250$ Å and $\varepsilon = 0.71145$ kJ/mol; for carbon $\sigma = 3.50$ Å and $\varepsilon = 0.27621$ kJ/mol; for hydrogen $\sigma = 2.50$ Å and $\varepsilon = 0.12555$ kJ/mol and for bromine $\sigma = 4.280$ Å, $\varepsilon = 2.97$ kJ/mol. Charges were placed only on nitrogen and bromine atoms, $q_N = +1$ |e|, $q_{Br} = -1$ |e|.

Simulation of dynamic properties was performed within lattice dynamic (LD) method in which quasi-harmonic approximation was used to find phonon spectrum and phonon density of states [9]. After calculations of potential energy and vibration spectrum, one can find Helmholtz free energy in a series of unit cell volumes: $F(V, T) = U + F_{\text{vib}}$. Part of free energy which depends on frequencies may be found from next general equation:
Pressure and equation of state may be found by numerical differentiation of the free energy by volume:

\[ P(V,T) = -\left( \frac{\partial F(V,T)}{\partial V} \right) \]  

(3)

Thermal expansion can be determined using this equation at \( P(V) \) of about zero at different temperatures. More detailed information about the lattice dynamics method may be found in [10,11].

3. Results

The dynamical stability means that all molecules are located at equilibrium positions and thus there are no complex frequencies of molecular vibrations. Using the proposed approach the positions of molecules in unit cells with different volumes and minimal energies were determined. After that the phonon densities of states were found at different volumes (figure 2a). In the figure 2b the phonon density of states for true clathrate hydrate of cubic structure 1 is presented for comparison.

![Figure 2](image)

**Figure 2.** Phonon density of states (PDOS) for (a) TBAB ICH and (b) clathrate hydrate cubic structure 1.

Presented PDOS demonstrate both similarity and difference in dynamical properties of these hydrates. At frequencies from about 500 cm\(^{-1}\) to 1000 cm\(^{-1}\), which are characteristic for rotational vibrations of water molecules, spectra are similar, and the differences are connected first of all with structural peculiarities of water cages. In the region of translation vibrations of water molecules one can also see similar behavior of PDOS, but a little higher number of low frequencies is connected with slow vibrations of tetrabutylammonium within water network. The most notable difference however may be seen in the region between about 330 cm\(^{-1}\) to 500 cm\(^{-1}\) i.e. in the “gap” which presents in “true” clathrate hydrates and ices. In this region of TBAB ICH the vibration density is non-zero as it demonstrated on figure 2a. We suppose that this is due to strong interaction between bromide anion that is embedded into water network and hardly influence the surrounding water molecules. Despite
these differences, phonon spectra of TBAB ICH is similar to that of “true” clathrate hydrate and demonstrates dynamical stability of this compound.

Calculations of free energy for TBAB ICH were performed in the range of unit cell volumes from 3650 to 3900 cm$^{-1}$ and temperature range 230 K to 283 K. The temperatures were chosen so, that they allow understanding the behavior of free energy at relatively soft conditions, i.e. conditions that are realized on Earth surface at atmospheric pressure. Quasi-harmonic approximation allows one to find Helmholtz free energy of a system at considered conditions. Figure 3 demonstrates the dependence of free energy on volume at temperature of ice melting conditions.

![Figure 3](image-url)  
**Figure 3.** The dependence of calculated free energy on volume, $F(V)$ at temperature $T = 273$ K.

The points on the graph $F(V)$ at given temperature can be well approximated by parabola. The minus derivative of this function is a pressure as it is shown in formulae (3). The same curves were built for all considered temperatures and the minimum of free energies depending on volume was determined. Figure 4 demonstrates the dependence of minimums of free energy by temperature.

The curve $F_{\text{min}}(T)$ is almost linear. When the temperature increases the free energy goes down. In the range from 230 K to 283 K free energy changes from -59.8 kJ/mol to -62.1 kJ/mol. It means that the vibration part of free energy plays an important role in thermodynamic properties of the TBAB ICH as it was earlier shown for true clathrate hydrates and other condensed phases of water.

![Figure 4](image-url)  
**Figure 4.** The dependence of free energy minimum on temperature.
Thermal expansion is the complex characteristic of compound that depends on free energy behavior against volume and temperature. It is influenced by both intermolecular potential interaction and lattice vibration. Figure 5 shows the calculated curve of relative volume, i.e. volume of unit cell normalized on cell volume at 230 K depending on temperature. The same curve for ice Ih is presented in the figure for comparison.

![Figure 5](image.png)

**Figure 5.** Thermal expansion of TBAB ICH and ice Ih, relative volume normalized to 230 K’ volume.

Volume $V(T)$ almost linearly grows with temperature increase. The relative volume of hydrate grows more rapidly than that of ice Ih and this means that for TBAB ICH self-preservation effect may be realized as for numerous gas hydrates.

**Conclusion**

Thermodynamic and dynamic properties of TBAB clathrate hydrate were investigated using the lattice dynamics method. The features in phonon density of states which can be explained as a result of interaction between TBAB and water molecules have been find. Free energy dependence on temperature in the range of 230 K – 283 K and its almost linear behavior has been determined. Relative thermal expansion of TBAB hydrate has been calculated and the expansion is shown to rise more rapidly than that of ice. On this basis the conclusion about self-preservation possibility for such complex compounds has been made. The obtained results will open new prospects for experimental and theoretical study of mixed non-classical TBAB gas hydrates.

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