Theoretical study of the self-preservation effect in CF₄ gas hydrates

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Abstract. This work studies thermodynamic properties of CF₄ gas hydrates using the statistical thermodynamic model of inclusion compounds, developed in our laboratory and closely associated with Quasiharmonic Lattice Dynamic (QLD) and Molecular Dynamic Simulation (MD). Thermal expansion coefficient of CF₄ gas hydrate is calculated at different hydrate composition. The thermal expansion coefficient is shown to be lesser than the thermal expansion coefficient of CH₄ hydrates, but larger than ice Ih, that still indicates the presence of the self-preservation effect. The thermal expansion coefficient is very sensitive to the composition of the hydrate and can vary in a wide range. The same is true for the hydrate lattice parameter as well; it is shown that at certain conditions it may be even less than for hypothetical empty hydrate structure. The self-preservation effect may be applied for many aspects related to CF₄ compound, especially for storage and transportation purposes in producing semiconductor electronics.

1. Introduction
Gas hydrates (clathrate hydrates) are non-stoichiometric crystalline compounds formed by water molecules and guest molecules with suitable size. At certain thermodynamic conditions (high pressure and/or low temperature) they are entrapped in cavities present in the hydrate crystal structure. Depending on the guest molecule type one of the following three clathrate structures are usually formed: cubic structure I (sI), cubic structure II (sII), and hexagonal structure III (sH). Gas hydrates may be spontaneously formed in gas transition systems (pipes), in crude oil processing infrastructure, etc., and can cause significant technical problems [1]. At the same time gas hydrates are usable for storage, transportation, gas separation, carbon dioxide trapping, saline water desalination, and many other purposes [2].

It has been found that some gas hydrates have abnormal low dissociation rate outside their zone of thermodynamic stability but at temperature below ice freezing point. This effect is called as “self-preservation effect” [3] and eventually has been found for many gas hydrate types. With this effect it is possible to significantly improve applicability of gas hydrates for gas storage purposes. At present, most of research papers deal only with the general nature of the self-preservation effect and do not focus on peculiar properties of specific gas.

Carbon tetrafluoride (CF₄) at present has many industrial applications, in particular, in semiconductor microelectronics manufacturing.
In this work we conduct theoretical investigation of carbon tetrafluoride hydrates outside the thermodynamic stability region to deepen our understanding of the self-preservation effect. This task is accomplished using a combination of QLD and MD methods closely related to the theoretical model of inclusion compounds [4]. The main focus of the present research work is on thermal expansion coefficient of the gas hydrate and its dependence on the hydrate composition.

2. Computational details

Our previous works about the self-preservation effect in different gas hydrates, all details of the models and model application were already described [4-6]. So, it is worth mentioning only the most important facts here. The main parameter of interest was the hydrate unit cell parameter dependence on temperature, since it could be directly recalculated into the linear thermal expansion coefficient. Using Molecular Dynamic methods we obtained equilibrated and minimized structures with different volumes. Then the Quasiharmonic Lattice Dynamic method was used for reconstructing free energy of these systems as one of the basic thermodynamic potentials that allow obtaining many thermodynamic properties of the system, and finally processing all the data in statistical thermodynamic theory of inclusion compounds developed in our laboratory [4].

Carbon tetrafluoride produces cubic structure I (sI) gas hydrate. Therefore, we used only this structure in our calculation. The sI hydrate unit cell consists of 46 water molecules with 2 small \((5^{12})\) cavities and 6 large \((5^{12}6^2)\) cavities. CF\(_4\) molecule can fit in the both cavity types.

Water molecules were described by modified SPC/E rigid model [7]. Potential of CF\(_4\) molecules was described by only 6-12 spherical symmetric Lennard-Jones potential with \(\sigma = 4.7\) Å and \(\varepsilon = 1.267\) kJ/mol [8].

3. Results and Discussion

The key factor that governs self-preservation effect is the difference of thermal expansion of gas hydrate and ice Ih phase. Right after extracting a hydrate from thermodynamic stability zone, the dissociation process starts with forming of ice Ih phase on the hydrate surface. The ice phase is strongly connected with the immersed hydrate phase, therefore, these two phases should have identical absolute thermal expansion. Because of the difference of thermal expansion coefficients, the additional pressure in the system is created [4].

Fig. 1 presents the dependence of unit cell parameters of empty sI hydrate structure and carbon tetrafluoride sI hydrate with occupation of different cages: only small cavities (0S), only large cavities (L0), and large and small cavities (LS) on temperature at constant pressure 1 bar. According to the obtained data occupation of different cage-types of cavities has different impact on the cell parameter. CF\(_4\) molecule is well fitted in a small cavity, and vDW interactions slightly expand the cavity itself and therefore expand the whole structure; even sI structure has only 2 small cavities. For only large cavities occupied by CF\(_4\) the molecule behavior is different. In comparison with the empty structure, the unit cell shrinks in the low temperature region and in the high temperature region it expands. This behavior can be explained by the vibration of the guests inside the cavities. Large cavity is slightly bigger than CF\(_4\) guest. In the low temperature region when vibration amplitude is low, CF\(_4\) are pulled together by vDW forces of nearest water molecules, composing a large cavity, and cause unit cell reduction. In the high temperature region vibration amplitude becomes larger and the guest efficiently occupies the entire cavity and, therefore, expands it together with the unit cell of hydrate. For both cavities occupied the behavior is just the sum of L0 and 0S cases.

According to our calculations possible values of unit cell may vary in a wide range for one temperature. Therefore, it is very important to control the composition of the hydrate for accurate determination of the unit cell parameter, especially using experimental methods. On the other hand, our data allow estimating the possible composition range of the hydrate using only unit cell parameter data obtained experimentally.
Figure 1. Unit cell parameter dependence on temperature for empty sI hydrate structure and CF$_4$ hydrate with occupation of different cages: only small cavities (0S), only large cavities (L0) and large and small cavities (LS).

Figure 2. Linear thermal expansion coefficient dependence on temperature for ice Ih, empty sI and sII hydrates, CH$_4$ sI hydrate, and CF$_4$ sI hydrate with occupation of different cages: only small cavities (0S), only large cavities (L0), and large and small cavities (LS).

Using calculated unit cell parameter data we obtained coefficient of thermal expansion for CF$_4$ hydrate and compared it with different coefficients. Fig. 2 presents dependence of linear thermal expansion of ice Ih, empty sI and sII hydrate structures, methane sI hydrate, and carbon tetrafluoride sI hydrate with occupation of different cages: only small cavities (0S), only large cavities (L0), and large and small cavities (LS) on temperature at constant pressure of 1 bar. The thermal expansion coefficient strongly depends on the composition of the hydrate: higher occupation rate gives larger thermal expansion coefficient. Unlike the unit cell parameter the thermal expansion coefficient is never less than that of the empty structure. According to our calculations the difference of thermal expansion of CF$_4$ (LS) hydrate and ice Ih is about 2 times lesser than for CH$_4$ hydrate, but very close to one of
carbon dioxide or hydrogen hydrates, nevertheless, it is enough to expect the self-preservation effect for carbon tetrafluoride.

Conclusions
In the presented work, the unit cell parameter and thermal expansion coefficient of carbon tetrafluoride sl gas hydrate have been calculated in a wide temperature range at constant pressure of 1 bar. Carbon tetrafluoride hydrate thermal expansion is shown to be larger than that of ice Ih or empty sl and sII structures. According to the calculated data the unit cell parameter as well as thermal expansion coefficient strongly depends on the hydrate composition and may vary in a wide range. Moreover, it has been shown that at temperatures below 110 K it is possible to observe the unit cell parameter of CF₄ hydrate lesser than that of the empty structure.

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