Theoretical investigation of nitrogen gas hydrates outside of stability zone

R K Zhdanov1,2, K V Gets1,2, Y Y Bozhko1,2, O S Subbotin1,2 and V R Belosludov1,2

1Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, 3 Lavrentiev Ave., Novosibirsk, Russia
2Novosibirsk State University, 630090, 2 Pirogov Street, Novosibirsk, Russia

E-mail: rav@niic.nsc.ru

Abstract. Using a combination of Quasiharmonic Lattice Dynamic and Molecular Dynamic Simulation methods in conjunction with well developed statistical thermodynamics theory the thermodynamic properties of nitrogen gas hydrates has been calculated, with the main focus on the thermal expansion coefficient. It is shown that nitrogen gas hydrate displays larger value of the thermal expansion coefficient in comparison with hexagonal ice Ih and empty gas hydrate lattice, moreover this value is very close to one of the carbon dioxide and to other hydrates that have self-preservation effect. Exactly because of this difference in the thermal expansion coefficient it is possible to confirm existence of the self-preservation effect. The self-preservation effect can be used for creation of low-cost technology of hydrates storage and transportation technology applicable for many gas types.

1. Introduction

Clathrate hydrates also known as gas hydrates are host-guest inclusion compounds that are crystalline materials consisting of water molecules that incorporate guest molecules inside hydrogen-bonded water cages [1]. Clathrate hydrates can be formed by many types of gases including natural gas. Usually in order to form a gas hydrate, high pressure and/or low temperature is required. But during continuous research it has been found that gas hydrates formed by certain gases (e.g. methane, ethane, carbon dioxide, etc.) had unexpectedly low decomposition speed after reducing ambient pressure to the atmospheric value. At first this effect has been reported by Yakushev and Istomin [2]. According to the following research it has been confirmed that certain hydrates display very low decomposition speed outside of the zone of their thermodynamic stability, but at temperatures below ice melting point (273 K), this behavior was called “self-preservation” effect or “anomalous preservation” [3]. Utilizing the self-preservation effect in industry could be considered as a possible solution for gas transportation problem at short distances where conventional pipe lines are not applicable, especially in case of delivery for end-point consumers. Also self-preservation effect is very important due to ecological problems modern society has faced in the recent decades [4].

The present research work aims at theoretical investigation of nitrogen gas hydrates outside thermodynamic stability region to improve our understanding of the self-preservation effect in nitrogen gas hydrates. In order to accomplish this task we used a combination of previously developed theoretical model, Quasiharmonic Lattice Dynamic approach, and Molecular Dynamic methods [5].
Since the main parameter responsible for the self-preservation effect is thermal expansion coefficient, we strongly focused on this parameter in this work.

2. Computational details
We assume that the main mechanism responsible for the self preservation effect is formation of an ice layer on the surface of the gas hydrate bulk phase due to the initial melting. Because ice phase and hydrate phase have different thermal expansion coefficients it causes a creation of an additional internal pressure in the hydrate that effectively returns the hydrate system back into stability zone [5,6]. The detailed description of this assumption can be found in our previous papers [5,6]. Here we are going to briefly describe the basic idea.

With the statistical thermodynamic model of inclusion compounds developed previously in our group is utilized in connection with Quasiharmonic Lattice Dynamic approach it is possible to obtain the Helmholtz free energy as function of temperature and volume or pressure. Using free energy it is possible to calculate any other required thermodynamic parameter of the system.

Because this paper is focused on thermal expansion, the equation for the coefficient of thermal expansion is:

$$a = \left( \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right)$$

The used gas hydrate model is based on molecular level description and many parameters are calculated from direct calculation of energies and interactions between water molecules and gas particles. The H$_2$O molecule in our calculation is described by a modified Simple Point Charge Extended (SPC/E) potential with parameters presented in our previous study [7]. This potential has been modified for better description of the thermal expansion of H$_2$O solid phases and proved its applicability for calculation of physical parameters and composition of gas hydrates. N$_2$ molecule was considered as a spherical particle with only van der Waals interaction described by Lennard-Jones potential with parameters from work [8].

3. Results and discussion
As it was mentioned previously the difference in the thermal expansion of the hydrate phase and ice phase that are formed on the hydrate surface is responsible for the appearance of the self-preservation effect, therefore, this is the parameter that should be calculated at first. Because the self-preservation effect is observable at atmospheric pressure we should calculate thermal expansion of all required systems at atmospheric pressure too. But in case of gas hydrates, thermal expansion strongly depends on the occupation of hydrate cavities by gas particles. Therefore, in order to calculate the thermal expansion we used occupation at hydrate formation pressure for each temperature point. Such approach is reasonable because hydrate decomposition start from the surface while the most part of the hydrate persists and the hydrate composition remains the almost the same as before decomposition process start.

Fig. 1 presents the calculated coefficient of thermal expansion of ice Ih phase, empty CS-I hydrate lattice, carbon dioxide CS-I hydrate, methane CS-I hydrate, and nitrogen CS-II hydrate depending on temperature at atmospheric pressure. The thermal expansions of methane, carbon dioxide, empty structures and ice Ih were calculated based on our previous data.
Figure 1. Temperature dependence of coefficient of thermal expansion for ice Ih structure, empty CS-I hydrate lattice, carbon dioxide CS-I hydrate, methane CS-I hydrate, and nitrogen CS-II hydrate.

For validation purposes we compared temperature dependence of unit cell parameter of the nitrogen hydrate with data presented by different research groups [9]. It has been found that our results do match other data, and therefore may be considered as valid.

As it was expected calculated thermal expansion coefficient of nitrogen gas hydrate is larger than thermal expansion of ice Ih, and the value is very close to the thermal expansion coefficient of the carbon dioxide hydrate (Fig. 1). In comparison with methane hydrates that display the largest thermal expansion parameter, nitrogen hydrates’ thermal expansion is 2 times smaller. Despite this the difference in the thermal expansions is still sufficient to cause the self-preservation effect even though the formation pressure for nitrogen hydrates is the highest among the presented gas hydrates.

Conclusions
In the presented work we applied the previously developed and well tested approach to calculate thermodynamic parameters of inclusion compounds outside the zone of their thermodynamic stability using nitrogen clathrate gas hydrates as our base target. It has been shown the coefficient of thermal expansion of nitrogen hydrates is larger than that for empty clathrate structure and ice Ih. Moreover, the absolute value is very close to one of the carbon dioxide and compatible with methane. In other words the self-preservation effect for nitrogen gas hydrates is governed by the mechanism revealed by the authors.

Acknowledgments
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