Clathrate hydrates — efficient and clean energy resource

Paweł Siuda, Joanna Sadlej

University of Warsaw, Faculty of Chemistry, Pasteur 1, 02-093 Warsaw, Poland,
e-mail: siuda.pawel@gmail.com

Clathrate hydrates are icelike structures in which water molecules form cavities enclathrating many possible types of guest molecules. Among most important representatives of this group of solid structures are methane and carbon dioxide clathrate hydrates. The first one is widely present in Nature and in the future will serve as an energy resource. Carbon dioxide clathrate hydrate may on the other hand serve as a storage reservoir for this green house gas providing cheap way to lower its emission to atmosphere.

Those are just two of many more important issues that catalyse growing interest of scientific world in clathrate hydrates. Characterisation of their properties is crucial to develop technologies, that will enable us to utilize their manifold possible applications. During this presentation I will discuss some of my investigations concerning NMR properties of clathrate hydrates.

Keywords and phrases: clathrate hydrates, energy, NMR.

Introduction

Clathrate hydrates are inclusion compounds based on water molecules forming three dimensional lattices. Guest molecules are encaged by the cavities in this lattice. Many different molecules could stabilize the structure as guests. Depending on their size and chemical character many different structures are possible. There are three most abundant types of structures named sI, sII and sH [1]. Structure of the first type is formed by smallest molecules, for example methane and ethane. Two types of cages serve as building blocks for this structure — 5^{12} and $5^{12}6^{2}$ cages. First one consists of twelve pentagons, while the second one is formed by twelve pentagons and two hexagons. Structures of those cages are depicted in Fig. 1 and 2.

Other types of structures (sII and sH) are stabilized by bigger guest molecules and consist of different types of cages. They can also be formed by mixtures of guest molecules. Cages that form crystal structure are of different size, so mixtures of molecules that differ in size are good hydrate formers. Not all of the cages must be filled with guest molecules to ensure overall stability of the crystal.

The actual type of crystal structure obtained depends not only on types and composition of guest molecules, but also on thermodynamic parameters of the system. Most important parameter is the pressure. Phase diagrams, describing structure of the hydrate depending on the temperature and pressure can be very complicated, especially for mixed hydrates, where the composition of guest molecules is additional factor.

Methane clathrate hydrate

Most important and most thoroughly investigated clathrate hydrate is methane clathrate hydrate. Great interest of scientists from many backgrounds is connected with unusual properties and abundance of this structure. Although it looks like normal ice, it contains about 164 volumes of methane in one volume of crystal [1]. This amount of methane is enough to burn hydrate, what is a very spectacular phenomenon. Another important property of methane clathrate hydrate is its stability in temperatures and pressures close to standard conditions, what is illustrated at Fig. 3. What is more, even small addition of propane can substantially lower stability pressure for methane clathrate hydrate. And still

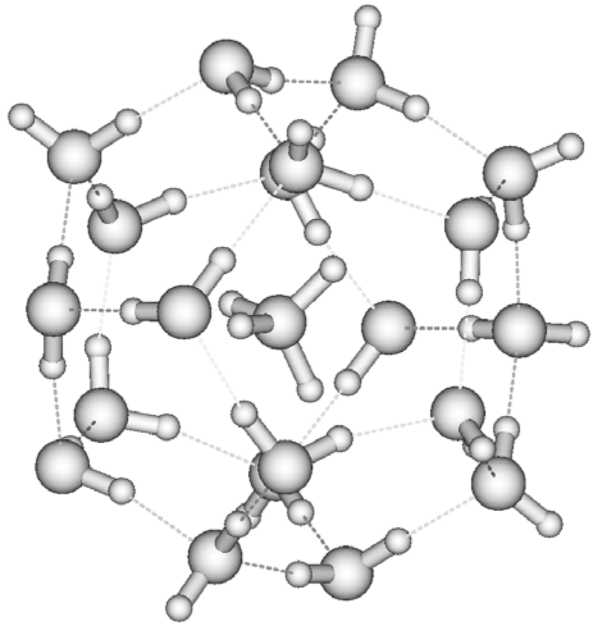

Fig. 1. 5^{12} cage of methane clathrate hydrate.

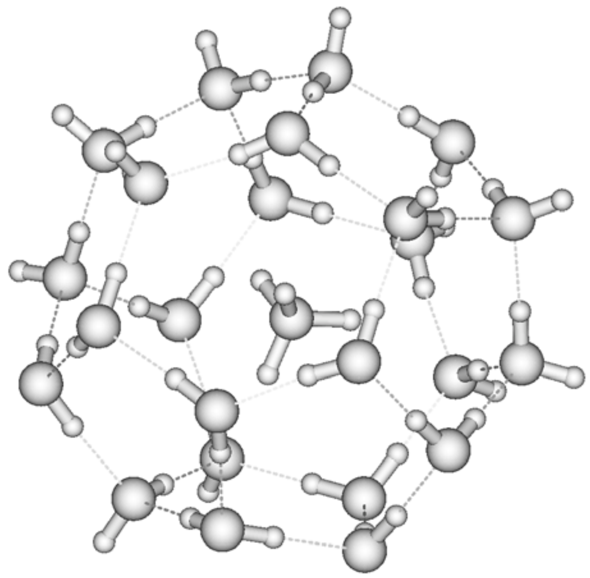

Fig. 2. $5^{12}6^{2}$ cage of methane clathrate hydrate.

more — once formed, methane clathrate hydrate has a broad region of metastability and under atmospheric pressure can persist for substantial period of time well above 0°C.

Special properties listed above and the fact, that methane clathrate hydrate is ubiquitous on Earth (arctic and permafrost regions of North America and Eurasia, all continental shelves) makes it very promising energy resource. Figure 4 presents proven reserves of methane clathrate hydrate located on oceans floors [3].

Methane is the cleanest and most effective fossil fuel and its role in global energy production is very important, as can be seen in Fig. 5, and in near future will be rapidly growing.

In recent years we are observing what can be called a shale gas revolution. United States has become greatest global producer of natural gas thank to boosting shale gas production. The resources of shale gas worldwide are huge (Poland has greatest reserves in Europe) and in nearest future they will change the global balance of energy, but in longer perspective hydrate could become even more important. Comparison of reserves of gas deposited in the form of clathrate hydrate, shale gas and in conventional resources are presented in Table 1.

Table 1. Reserves of gas resources on Earth.

Energy resource	Global reserves (mld m^3)
Conventional natural gas	180 000[5]
Shale gas	450 000[5]
Hydrate gas	100 000 000[3]

Seeing the potential of methane clathrate hydrate as energy resource many countries invest heavily in development of technologies needed to utilize it. As hydrate deposits are located in greatest abundance on ocean's floors and are dispersed in sediments it is still a great technical challenge that must be surmounted. However, even if just a small fraction of methane hydrate reserves would become economically viable to produce methane, that would affect world energy market dramatically and brought billions of dollars to the owner of suitable technology.

Carbon dioxide clathrate hydrate

Carbon dioxide clathrate hydrate is the second most important representative of clathrate hydrates. Interestingly, it was was first discovered by Jagiellonian University professor Zygmunt Wróblewski in 1882 in Krakow. The structure of CO_2 clathrate hydrate is the same as for methane, namely sI. The thermodynamic stability zone is also similar, but carbon dioxide clathrate is more stable than methane clathrate.

Importance of carbon dioxide clathrate hydrate is connected with its stability. Starting from the Kyoto Protocol assignment in 1997 reduction of carbon dioxide emissions is needed in many countries. An efficient, secure and cheap technology is needed to store CO_2 not to let it being emitted into the atmosphere. Clathrate hydrates of carbon dioxide may be an option.

More complex idea is to use carbon dioxide hydrate both as a mean to sequester CO_2 and to produce methane from methane clathrate hydrates at the same time [6, 7]. Addition of liquid CO_2 into methane clathrate hydrate

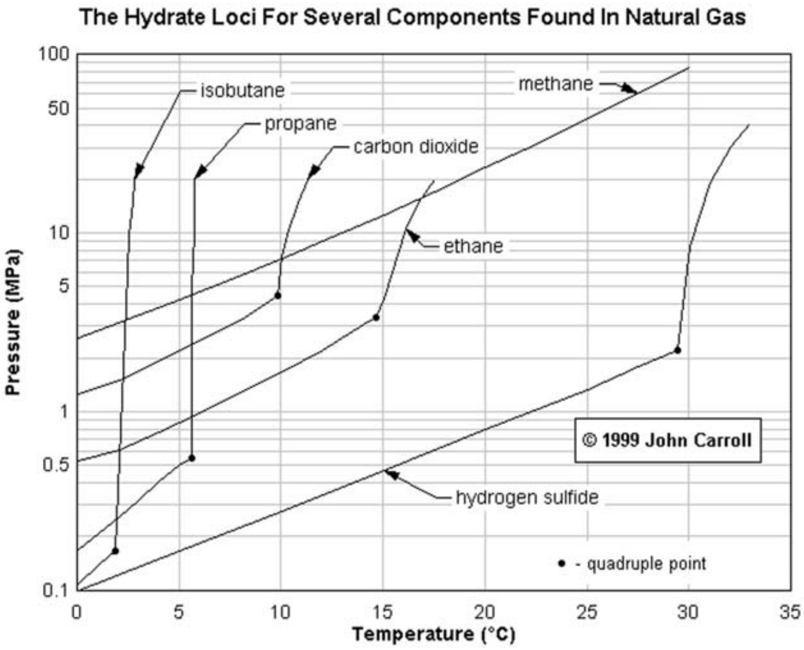

Fig. 3. Phase diagram of most important clathrate hydrate formers [2].

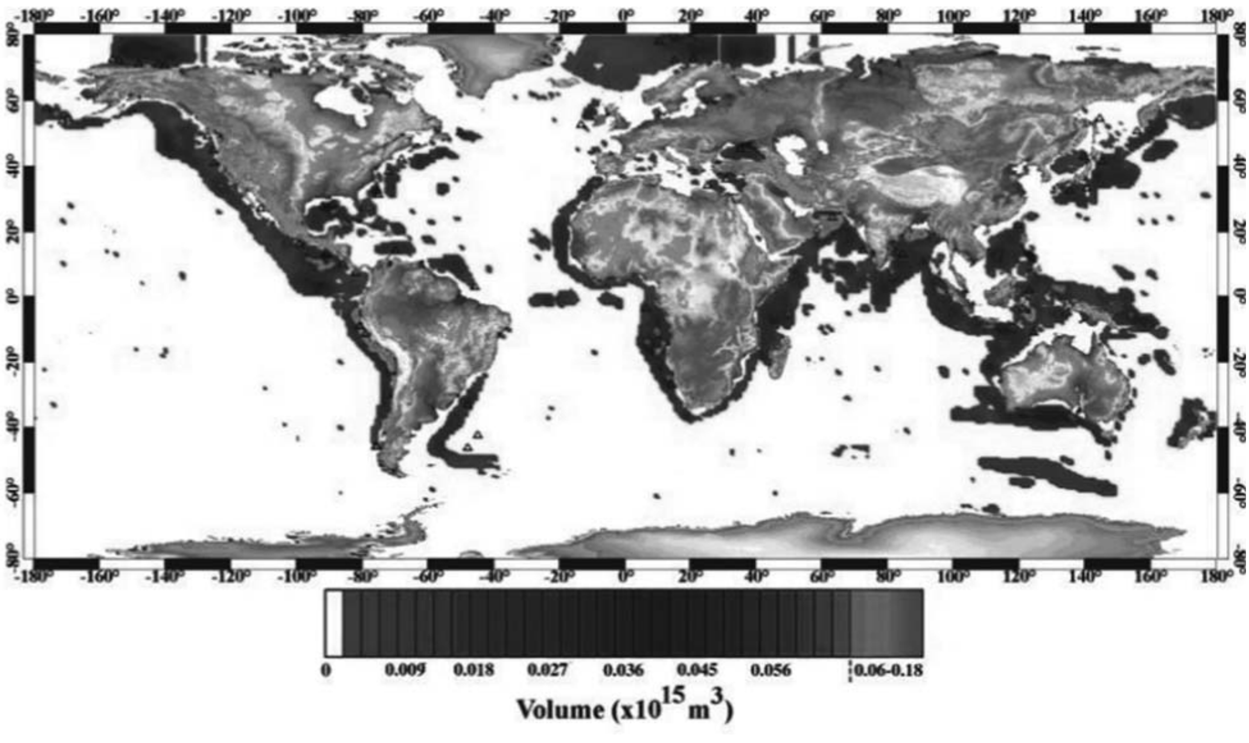

Fig. 4. Locations of proven methane clathrate hydrate reservoirs.

reservoir should lead to conversion of methane clathrate hydrate into carbon dioxide clathrate hydrate. Methane should be released from the reservoir and collected. It could be for example burned to produce energy and generated CO_2 after liquefaction could be used again to produce more methane. In this way we would have an ecologically clean source of energy, with CO_2 safely sequestered in ocean's depths.

Calculations of NMR properties of clathrate hydrates

My research is devoted to determination of NMR properties of clathrate hydrates of hydrocarbons and carbon dioxide. I am using computational methods of quantum chemistry at the highest currently applicable to such a big systems level of theory. It is Density

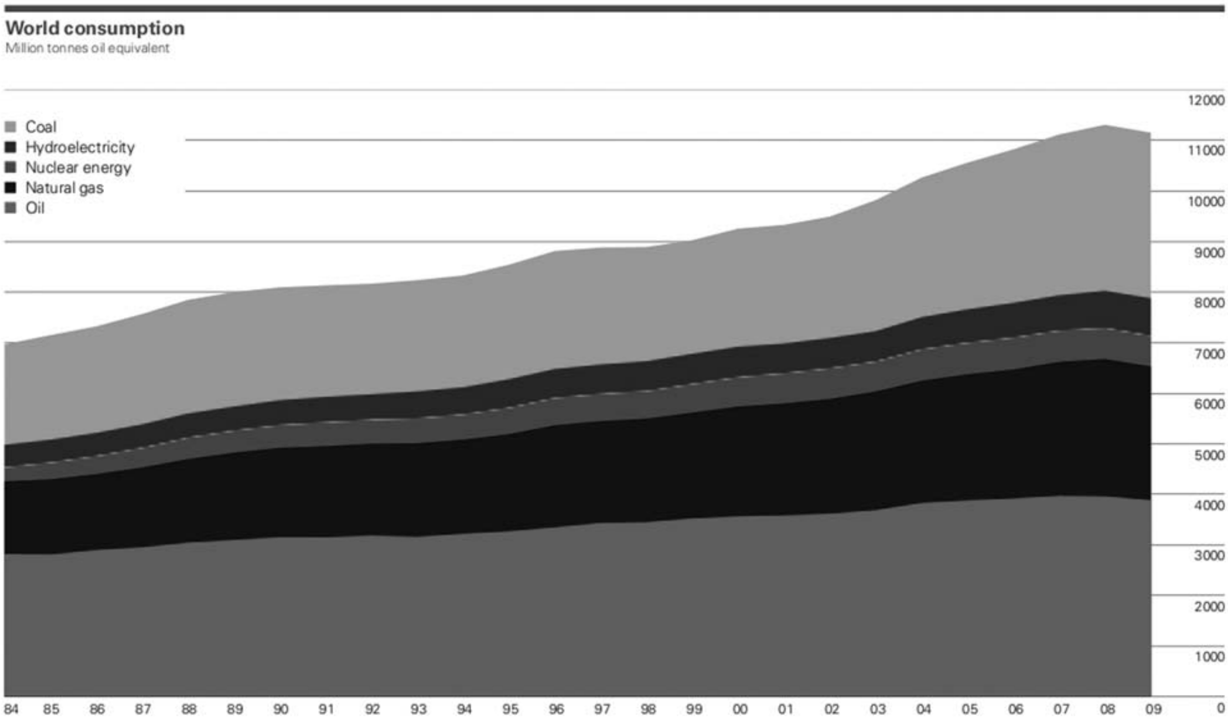

Fig. 5. World energy consumption [4].

Functional Theory with hybrid B3LYP functional and devoted to NMR calculations extensive basis set HuzIII-su3.

The use of NMR to characterize clathrate hydrates can answer several important questions. The amount of methane present in the deposit depends on the type of structure of the hydrate and on the of occupation of accessible cages in the hydrate structure by quest molecules. Both could be determined by NMR technic. Up to just few years ago it was believed, that most of the global methane clathrate deposits contain sI type of structure. Nowadays there are more evidences, that sII structure may be widely present too. NMR provides simple way to determine whether particular sample is of sI or sII type. This is due to the fact, that methane molecules present in different types of cages forming those structures have different chemical shifts.

Another important issue is the occupation of accessible cages by quest molecules. To assess how much methane is stored in deposit it is important to know whether all the cages are occupied or not. Intensity of NMR signal may help to estimate this property with high level of accuracy.

NMR can also answer the question of composition of quest molecules. Natural deposits of methane clathrate hydrates always contain several percent of additions. The most abundant additions are ethane and propane molecules, but many others are also possible. Even small addition of ethane and/or propane dramatically changes the stability of the clathrate hydrate crystal. This fact must be considered during development of technologies suitable to methane extraction from the clathrate hydrate. As chemical shifts of atoms forming guest molecules can be determined, NMR may be utilised in determination of exact composition of guest molecules in particular occurence of clathrate hydrate.

Table 2 containes results of my calculations for carbon dioxide clathrate hydrates of sI structure. One important thing is, that although the differences in chemical shifts of carbon seem to be small thay are big enough to unambiguously distinguish between molecules encaged by bigger and smaller cages. This is helpful in two occacions mentioned before. In the first place —

Table 2. Comparison of experimental and computational (DFT/B3LYP/HuzIII-su3) results for ^{13}C chemical shift in carbon dioxide sI clathrate hydrate (all in ppm).

CO_2 in:	Experimantal results	My calculations	Experimental results rescalled	My calculations rescalled
gas phase	126.0 [8]	46.3	0.0	0.0
5^{12} cage	123.1 [9]	45.2	-2.9	-1.1
$5^{12}6^2$ cage	127.8 [9]	48.3	1.8	2.0

it proves that we really can distinguish between cages, so also between different structures of the clathrate hydrate. Secondly — we can use this data to assess the occupancy of each type of cage present in the clathrate hydrate structure and the overall occupancy as well.

The comparison of experimental and computational results shows, that it is possible today to predict computationally NMR parameters for clathrate hydrates with great accuracy. This is very important especially for more complicated systems present in nature, which may contain a mixture of many guests in any proportions. NMR parameters can unambiguously distinguish them and their concentrations in clathrate hydrates.

Conclusions

Clathrate hydrates are solid structures formed by H-bonded water molecules encaging guest molecules. It is easy to modulate their structural and thermodynamical properties by varying the quest molecule characteristics. Thank for this flexibility lots of possible applications are possible. Not only those mentioned above, like CO_2 storage, but also hydrogen storage, cold energy storage, gas separation, and many more.

Methane clathrate hydrate is believed to become a major energy source in the future. Amount of its reserves on Earth are so huge, that it could provide energy for many centuries. Technologies needed to utilize it are still to be developed. Research activity in this field is huge, so the next energetic revolution after shale gas revolution may come sooner than expected. Carbon dioxide may also play important role in this field as a reservoir for storage of this green house gas. Using methane from hydrate to generate energy and then store produced carbon dioxide in the form of clathrate hydrate is an ideal that we should quest for.

NMR parameters may be very useful in characterisation of important properties of clathrate hydrates. They can help to identify different quests present in the crystal, what is crucial for the stability requirements of the system. It is also possible to assess the occupation of cages by NMR technic what is also important for future technologies of utilization of methane clathrate hydrate as an energy resource. Computational methods provide accurate predictions of NMR properties of clathrate hydrates what is essential in interpretation of experimental results.

References

[1] Sloan, E.D., and C.A. Koh. *Clathrate Hydrates of Natural Gases*. New York: CRC Press, 2008.

[2] Wagner, W., and K.M. de Reuck. *Methane Thermodynamic Tables of the Fluid State — 13*. London: Blackwell Science, 1996.

[3] Klauda, J.B., and S.I. Sandler. „Global Distribution of Methane Hydrate in Ocean Sediment". *Energy Fuels* 19, (2005): 459.

[4] *World energy report*, BP, 2010.

[5] *US National Petroleum Council Report*, 2007.

[6] Tegze, G., L. Granasy, and B. Kvamme. „Phase field modeling of CH_4 hydrate conversion into CO_2 hydrate in the presence of liquid CO_2". *Physical Chemistry Chemical Physics* 9 (2007).

[7] Svandal, A., and B. Kvamme. „Modeling the dissociation of carbon dioxide and methane hydrate using the phase field theory". *Journal of Mathematical Chemistry* 46 (2009).

[8] Omi, H., et al. "Dynamics of CO_2 molecules confined in the micropores of silods as studied by ^{13}C NMR". *Applied Surface Science* 252 (2005).

[9] Seo, Y-T., and H. Lee. „Structure and guest distribution of the mixed carbon dioxide and nitrogen hydrates as revealed by X-ray diffraction and ^{13}C NMR spectroscopy". *Journal of Physical Chemistry B* 108 (2004).