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Thermodynamic Stability of Structure H Hydrates Based on the Molecular Properties of Large Guest Molecules

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Abstract: This paper report analyses of thermodynamic stability of structure-H clathrate hydrates formed with methane and large guest molecules in terms of their gas phase molecular sizes and molar masses for the selection of a large guest molecule providing better hydrate stability. We investigated the correlation among the gas phase molecular sizes, the molar masses of large molecule guest substances, and the equilibrium pressures. The results suggest that there exists a molecular-size value for the best stability. Also, at a given molecule size, better stability may be available when the large molecule guest substance has a larger molar mass.

Keywords: clathrate hydrate; structure H; phase equilibria; molecular properties

1. Introduction

Clathrate hydrates are crystalline inclusion compounds consisting of hydrogen-bonded water molecules forming cages that contain guest molecules [1]. There are variations in the crystallographic structures of hydrates, leading to structures designated as I, II and H, depending on the chemical species of the guest substances [1]. Structure-H hydrate forms with two different guest substances: one

is a small molecule guest substance, such as methane, xenon, and the other is a relatively large molecule guest substance (LMGS). Ripmeester and Ratcliffe have discovered a wide variety of LMGSs, such as 2-methylbutane and 2,2-dimethylbutane [2].

Phase-equilibrium conditions of structure-H hydrates are milder (*i.e.*, higher temperature/lower pressure) than those of structure-I or structure-II hydrates formed only with a small molecule guest substance. The milder phase equilibrium conditions in the structure-H hydrate forming systems is favorable for new technologies utilizing hydrates for storage (methane [3] or hydrogen [4,5]), capturing carbon dioxide [6], highly efficient heat pumps [7], *etc.*

For a given small-molecule guest substance, equilibrium pressures vary depending on the chemical species of the LMGSs. For example, at 276 K, the equilibrium pressure for the structure-H hydrate formed with methane and 2-methylbutane is 2.9 MPa [8]; while the formation pressure at 276 K is reduced to 1.6 MPa for the structure-H formed with methane and 2,2-dimethylbutane [9]. Although a number of phase-equilibrium data of structure-H hydrates with various LMGSs have been previously reported [5,8–15], there is no comprehensive understanding on the correlation between the thermodynamic stability of structure-H hydrates and the chemical species of the LMGSs. As for the structure I and II hydrates formed with a small molecule guests modeled with the Lennard-Jones potential, there seems a tendency that the hydrate stability increases with guest molecules having optimum molecular size and greater molar mass [16]. Specific chemical functionality in the molecule may alter these stability trends as the small guest molecules may interact differently with the host cage water molecules [17].

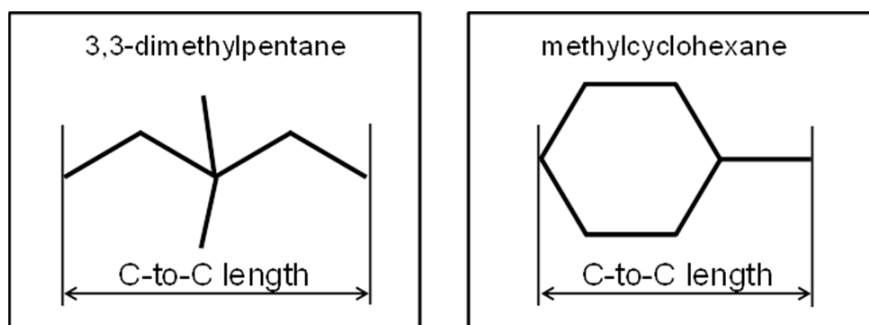
A recent computational study on structure-H hydrates looked at the stability of question for methane and various LMGSs by performing molecular dynamics (MD) simulations with a spherical one-site spherical Lennard-Jones (LJ) potential model for the LMGSs [18]. From this report, it was found that Gibbs energy difference ΔG tends to strongly depend on the effective LJ parameters (σ and ϵ) of the LMGSs. With appropriate values of σ , the structure-H hydrate with lower Gibbs energy is formed at larger values of ϵ based on contour lines of ΔG [19]. Based on these studies, it is expected that within chemically similar groups of guest molecules the equilibrium pressures of the structure-H hydrate may be correlated to the molecule size and molar mass of the LMGSs. Recently, Frankcombe and Kroes proposed a molecular simulation method to estimate the thermodynamic stability of the structure-H hydrates [19]. The implementations of molecular dynamics of hydrates [18] and the guest-host interaction energy calculations [19] require significant computation resources. Thus, it would be desirable if the hydrate stability depending on the chemical species of guests were predicted in a simpler manner.

In the present study, we study possible correlations between the thermodynamic stability of structure-H hydrates and the structure and functionality of a large group of chemical species of LMGS. Specifically, we quantitatively analyze the dependence of thermodynamic stability of structure-H hydrate on the molecular size of the isolated molecules as determined by different geometric criteria and molar mass of the LMGSs. Molecular sizes of the LMGSs reported in the literature are calculated with Gaussian03 quantum chemistry program [20]. We detail our approach and discuss the empirical relationships between the molecular size and the molar mass of the LMGSs and the thermodynamic stability.

2. Computational Method

To study correlations between the molecular size and thermodynamic stability, we use equilibrium pressure data of structure-H hydrates formed with methane and 20 different LMGSs, as reported in previous studies [8–15] and calculated from interpolation of the data at 276 K. The calculations of different criteria for LMGSs molecular size were performed using the Gaussian03 program. These involved to first optimize the geometry of the LMGSs with the hybrid density functional B3LYP method and aug-cc-pVDZ basis sets, followed by a calculation of the molecular volume and the longest distance between two carbon atoms in a large molecule guest substance. The maximum length was defined as “C-to-C length”, as shown Figure 1.

Figure 1. The definition of C-to-C length, which is the longest distance between two carbon atoms in a LMGS. Two molecules are shown are examples.



3. Results and Discussion

The correlations between the C-to-C length, the molecular volume, and the molar mass of LMGSs with the equilibrium pressures at 276 K are plotted in Figures 2–4. Please note that the same molecules appear on different parts of the x-axis in Figures 2–4. The guest molecules chosen in this study are alkanes, alkenes, alcohols, ethers, ketones. Some of the guests have roughly similar sizes, but differ by the position of the substituent group on the main carbon backbone of the molecule.

Figure 2 shows correlations between longest C-to-C length of the isolated guest molecules and the equilibrium pressure. The C-to-C lengths of LMGSs fall within the range of 3.0–5.5 Å. This figure suggests that the equilibrium pressure of structure-H hydrates is the lowest with the LMGS having C-to-C length of about 4.5 Å. LMGSs with smaller and larger C-to-C lengths than 4.5 Å require higher pressure to form. Figure 3 shows the correlation between molecular volume and the equilibrium pressure. The range of molecular volumes of LMGSs is 100–220 Å³. The correlation between formation pressure and C-to-C length shows less scatter than the volume plot given in Figure 3. As shown in Figure 3, the corresponding value of the molecular volume for the best stability is about 190 Å³. Figure 4 shows the correlation between molar mass and the equilibrium pressure. From the data in the figure, the lower equilibrium pressure may be for the LMGS having the largest molar mass. These results are consistent with the previous study on structure-H hydrate, which showed lower Gibbs energy is associated with appropriate values of σ representing the particle diameter and larger values of ϵ , positively correlated with molar mass [18].

Figure 2. Correlation plot between C-to-C length of LMGS and the equilibrium pressure at 276 K.

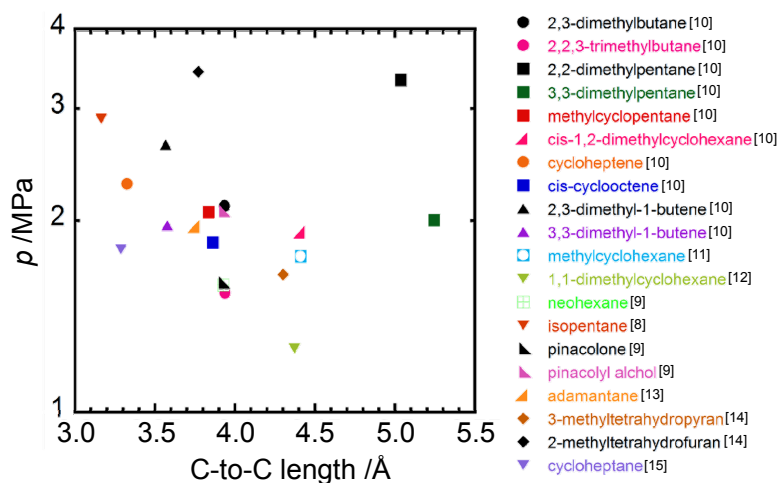


Figure 3. Correlation plot between molecular volume of LMGS and the equilibrium pressure at 276 K.

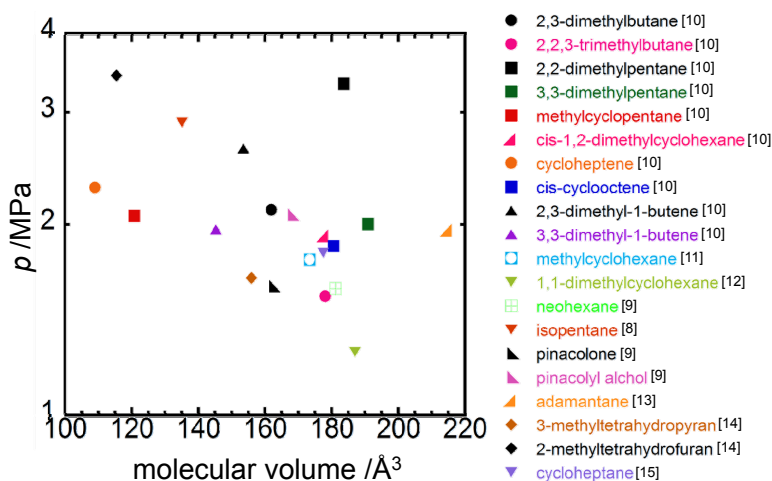
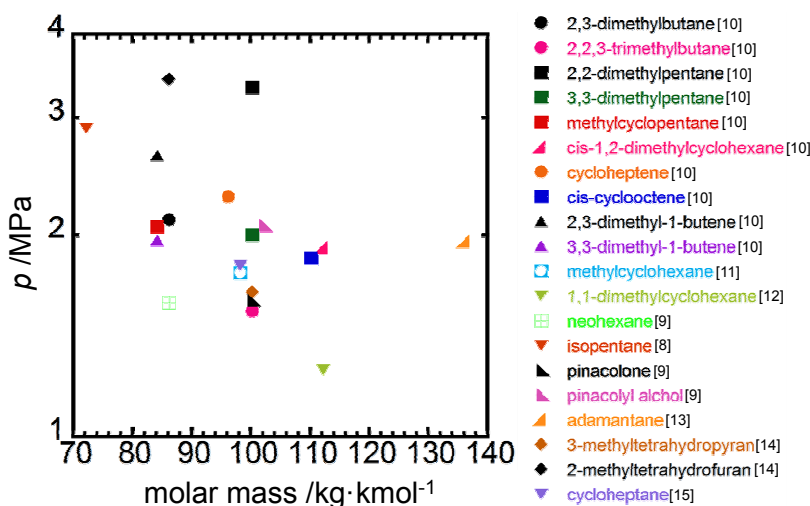


Figure 4. Correlation plot between molar mass of LMGS and the equilibrium pressure at 276 K.



Another feature on the stability of structure-H hydrate seen from Figure 4 is the relative stability of hydrates formed by isomeric molecules: 2,2-dimethylpentane and 3,3-dimethylpentane have the same molar mass (100.21 kg/kmol), but have different equilibrium pressure (3.3 MPa for 2,2-dimethylpentane, 2.0 MPa for 3,3-dimethylpentane).

Also, changes in the functional group from carbonyl to hydroxyl, e.g., pinacolone and pinacolyl alcohol, have a considerable effect on equilibrium pressure, 1.6 MPa for pinacolone and 2.1 MPa for pinacolyl alcohol, while differing slightly in their molecular sizes, which are 3.9 Å of C-to-C length for both, and 162 Å³ of molecular volume for pinacolone and 168 Å³ for pinacolyl alcohol, and molar masses, which are 100.16 kg/kmol for pinacolone and 102.18 kg/kmol for pinacolyl alcohol, as shown in Figures 2–4.

However, we also see that there are some data points in Figure 2–4 that deviate from these trends. This is because thermodynamic stability of structure-H hydrate is attributed to a complex combination of factors. One of factors includes the molecular shape of the LMGSs. For instance, we focus on 2,2-dimethylpentane and adamantane as the LMGS. In Figure 3, the equilibrium pressure of the structure-H hydrate formed with methane and 2,2-dimethylpentane is high (3.3 MPa), despite its molecular volume of approximate 190 Å³. However, if we look at the C-to-C length of 2,2-dimethylpentane of 5.0 Å, it is longer than the ideal length of 4.5 Å. Also, in Figure 4, the equilibrium pressure of the structure-H hydrate formed with methane and adamantane is not lower (1.9 MPa), despite the larger molar mass. This is because the C-to-C length of 3.7 Å is shorter than the ideal length of 4.5 Å and molecular volume of 215 Å³ is larger than the ideal volume of 190 Å³.

Another factor may be the methane content in the hydrates. Specially, the structure-H hydrates may not all have the same methane content. This is because the LMGSs have different mutual solubilities with water and methane, and so the access of the LMGSs and the hydrate phase to methane may be different. The difference of methane content may affect thermodynamic stability.

In summary, in terms of dependence of thermodynamic stability of structure-H hydrates on the C-to-C length, the molecular volume, and the molar mass of LMGSs, the most stable structure-H hydrates are formed with LMGSs that satisfies all of the following three conditions on their molecular properties: C-to-C length of about 4.5 Å, molecular volume of approximately 190 Å³, and large molar mass.

4. Concluding Remarks

We have calculated the molecular size and the molecular volume of LMGSs reported in the literature, and formulated empirical relationships between the molecular size and the molar mass of LMGSs and the thermodynamic stability. Structure-H hydrates are formed with guests within a limited C-to-C length ranging from 3.0 to 5.5 Å and molecular volume ranging from 100 to 220 Å³. These results suggest that the lowest equilibrium pressure for structure-H hydrates is formed with LMGS having C-to-C length of about 4.5 Å, molecular volume of approximately 190 Å³, and large molar mass. These results also indicate that isomer LMGSs have different equilibrium pressure, and changes in the functional group of the LMGS from carbonyl to hydroxyl affect thermodynamic stability.

The data analyses in the present study provide the general trend for the correlations between the C-to-C length, the molecular volume, and the molar mass of LMGSs with the equilibrium pressures,

but there is significant scattering in the correlations. The correlations alone are not conclusive and the stability is a complex combination of factors. The molecular structure of the LMGS is not rigid and can deform in the hydrate cage, affecting its effective size. Also, the stability depends on the shape of the molecule and cage so some criterion based on the ellipticity of the guest may be more appropriate than volume. These will be the subject of further studies.

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References

1. Sloan, E.D.; Koh, C.A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2008.
2. Ripmeester, J.A.; Ratcliffe, C.I. ^{129}Xe NMR studies of clathrate hydrates: New guests for structure I1 and structure H. *J. Phys. Chem.* **1990**, *94*, 8773–8776.
3. Mori, Y.H. Recent advances in hydrate-based technologies for natural gas storage—A review. *J. Chem. Ind. Eng. China* **2003**, *54*, 1–17.
4. Mao, W.L.; Mao, H. Hydrogen storage in molecular compounds. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 708–710.
5. Duarte, A.R.C.; Shariati, A.; Rovetto, L.J.; Peters, C.J. Water cavities of sH clathrate hydrate stabilized by molecular hydrogen: Phase equilibrium measurements. *J. Phys. Chem. B* **2008**, *112*, 1888–1889.
6. Seo, Y.T.; Moudravski, I.L.; Ripmeester, J.A.; Lee, J.W.; Lee, H. Efficient recovery of CO_2 from flue gas by clathrate hydrate formation in porous silica gels. *Environ. Sci. Technol.* **2005**, *39*, 2315–2319.
7. Ogawa, T.; Ito, T.; Watanabe, K.; Tahara, K.; Hiraoka, R.; Ochiai, J.; Ohmura, R.; Mori, Y.H. Development of a novel hydrate-based refrigeration system: A preliminary overview. *Appl. Therm. Eng.* **2006**, *26*, 2157–2167.
8. Mehta, A.P.; Sloan, E.D. Structure H hydrate phase equilibria of methane + liquid hydrocarbon mixtures. *J. Chem. Eng. Data* **1993**, *38*, 580–582.
9. Ohmura, R.; Uchida, T.; Takeya, S.; Nagao, J.; Minagawa, H.; Ebinuma, T.; Narita, H. Phase equilibrium for structure-H hydrates formed with methane and either pinacolone (3,3-dimethyl-2-butanone) or pinacolyl alcohol (3,3-dimethyl-2-butanol). *J. Chem. Eng. Data* **2004**, *48*, 1337–1340.
10. Mehta, A.P.; Sloan, E.D. Structure H hydrate phase equilibria of paraffins naphthenes, and olefins with methane. *J. Chem. Eng. Data* **1994**, *39*, 887–890.
11. Ohmura, R.; Uchida, T.; Takeya, S.; Nagao, J.; Minagawa, H.; Ebinuma, T.; Narita, H. Clathrate hydrate formation in (methane + water + methylcyclohexanone) systems: The first phase equilibrium data. *J. Chem. Thermodyn.* **2003**, *35*, 2045–2054.

12. Hara, T.; Hashimoto, S.; Sugahara, T.; Ohgaki, K. Large pressure depression of methane hydrate by adding 1,1-dimethylcyclohexane. *Chem. Eng. Sci.* **2005**, *60*, 3117–3119.
13. Hütz, U.; Englezos, P. Measurement of structure H hydrate phase equilibrium and effect of electrolytes. *Fluid Phase Equilib.* **1996**, *117*, 178–185.
14. Ohmura, R.; Matsuda, S.; Takeya, S.; Ebinuma, T.; Narita, H. Phase equilibrium for structure-H hydrates formed with methane and methyl-substituted cyclic ether. *Int. J. Thermophys.* **2005**, *5*, 1515–1523.
15. Kozaki, T.; Taguchi, T.; Takeya, S.; Ohmura, R. Phase equilibrium for structure H hydrates formed with methane plus cycloheptane, cycloheptanone or oxacycloheptane. *J. Chem. Eng. Data* **2010**, *55*, 3059–3062.
16. Miyoshi, T.; Imai, M.; Ohmura, R.; Yasuoka, K. Thermodynamic stability of type-I and type-II clathrate hydrates depending on the chemical species of the guest substances. *J. Chem. Phys.* **2007**, *126*, 234506:1–234506:6.
17. Alavi, S.; Susilo, R.; Ripmeester, J.A. Linking microscopic guest properties to macroscopic observables in clathrate hydrates: Guest-host hydrogen bonding. *J. Chem. Phys.* **2009**, *170*, 174501:1–174501:9.
18. Okano, Y.; Yasuoka, K. Free-energy calculation of structure-H hydrates. *J. Chem. Phys.* **2006**, *124*, 024510:1–024510:9.
19. Frankcombe, T.J.; Kroes, G.J. A new method for screening potential sII and sH hydrogen clathrate hydrate promoters with model potentials. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13410–13420.
20. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; *et al.* *GAUSSIAN 03*; Gaussian, Inc.: Pittsburgh, PA, USA, 2003.

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