Supporting information

Molecular Mechanism of the Inhibition Effects of PVCaps on the

Growth of sI Hydrate: Unstable Adsorption Mechanism

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1. The Simulation Details

1.1 Force Field Parameters

The water and methane molecules were described by TIP4P-Ew water model and OPLS-AA model [1-3], respectively. The atomic charges and L-J potential were shown in Table 1. Geometric combining rules were used for the Lennard-Jones cross-terms ($\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} \sigma_{jj})^{1/2}$), except that $\sigma = 3.032$ Å and $\varepsilon = 0.255$ kcal/mol (obtained by fitting to the QM calculated interactions by Cao et al.[4-5]) are used for O (of water) and C (of methane) interactions.

Table S1: The Parameters for L-J 12-6 Potential and Atomic Charges in this work

Element	Molecule	ε(kcal/mol)	σ(Å)	Charge
O	H_2O	0.163	3.164	
H		0.000	0.000	0.5242
M				-1.0484
C	CH_4	0.066	3.500	-0.2400
H		0.030	2.500	0.0600

The PVCap was described by OPLS-AA model [6]. The PVCaps' atomic charges and L-J potential were shown in Table 2 and Figure 1. Although the charges of the model we used had not been modified by QM, the amide oxygen charges were close to the parameters which were used by

QM calculation and the PVCaps' adsorption pattern was agree with the work by T. Yagasaki et al. [7]. These demonstrated the accuracy of parameters in our work.

Table S2: The PVCaps' Parameters for L-J 12-6 Potential and Atomic Charges in this work

Element	Molecule	ε(kcal/mol)	σ(Å)	Charge
C1	PVCaps	0.066	3.500	0.1200
C2		0.066	3.500	-0.1200
C3		0.066	3.500	-0.1800
C4		0.066	3.500	0.0600
C'		0.105	3.750	0.6000
O		0.210	2.960	-0.6000
N		0.170	3.250	-0.3600
H		0.030	2.500	0.0600

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[2] Y. T. Tung, L. J. Chen, Y. P. Chen and S. T. Lin, Journal of Physical Chemistry B, 2010, 114, 10804.

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[4] Z. T. Cao, J. W. Tester, K. A. Sparks and B. L. Trout, Journal of Physical Chemistry B, 2001, 105, 10950.

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[6] W. L. Jorgensen, D. S. M. And and J. Tiradorives, Journal of the American Chemical Society, 1996, 118, 11225-11236.

[7] T. Yagasaki, M. Matsumoto and H. Tanaka, Journal of the American Chemical Society, 2015, 137, 12079.

1.2 Water Rings Perception Algorithm

Ours water rings perception algorithm was referred the work of M. Matsumoto et al. **[8]**

a. Firstly, the hydrogen bonding between two oxygen (O_i and O_j) was determined by the two parameters in Figure 2 ($R_{ij} \leq 3.5$ Å and $\theta \leq 30°$).

b. Second, we built the map, shown in S1, between central oxygen (O_i) and the other oxygen (O_j) which can be connected with O_i by hydrogen bonding. Then we used the algorithm of traversing the tree to find the cyclic paths through these map information. When a cyclic path was found, all the cyclic paths were looked up and set in a stack.

$$O_i \rightarrow \begin{bmatrix} O_{j1} \\ O_{j2} \\ O_{j3} \\ O_{j4} \end{bmatrix}$$

[S1]

c. Finally, identical rings were eliminated from the stack, and the rings must be the shortest routes for the oxygen in these rings. The list of all distinguishable rings was obtained in the stack. We gave an example about the meaning of the shortest routes, shown in Figure 3. It means that if a 7-ring is composed by a 5-ring and 6-ring, the 7-ring can't be existing. The 5-ring and 6-ring are the shortest routes for these eight points.

[8] M. Matsumoto, A. Baba and I. Ohmine, Journal of Chemical Physics, 127, 134504 (2007).

1.3 Hydrate Identification Algorithm

The polyhedral cages (5^{12}, $5^{12}6^2$, $5^{12}6^4$ and $5^{12}6^3$) form the SI and SII hydrate crystals and metastable structure. Moreover, during the nucleation/growth of hydrate, there are some unclosed polyhedral cages in the system. These unclosed polyhedral cages are also regard as the preparative hydrate in our work to refine the region of hydrate. Therefore, the polyhedral cages were split into

smaller unit structures, shown in Figure 4. The algorithms sought for water "cups" which are local fragment of cages formed by pentagons and hexagons. Each pentagon/hexagon and its adjacent pentagons can form these cups in certain condition, so that we can define the unclosed cages. This way extends the range of hydrates recognition, comparing with the method of identification of complete cages structure. It helps to distinguish amorphous cages or metastable cages around the inhibitors, and to identify hydrates more completely.