Supporting Information

Methane Hydrates with a High Capacity and High Formation Rate Promoted by Biosurfactants

Weixing Wang,[1,*] Zhan Huang,[1] Haoran Chen,[2] Zhuyan Tan,[1] Caixing Chen,[1] Luyi Sun[2,*]

[1]Ministry of Education Key Laboratory of Enhanced Heat Transfer & Energy Conservation, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China 510640

[2]Department of Chemistry and Biochemistry & Materials Science, Engineering, and Commercialization Program, Texas State University–San Marcos, San Macros, TX 78666 USA

*Authors to whom correspondence should be addressed:

Dr. Weixing Wang, Tel: 8620-22236985; Fax: 8620-22236985; Email: cewxwang@scut.edu.cn

Dr. Luyi Sun, Tel: (512) 245-5563; Fax: (512) 245-2374; Email: luyi.sun@txstate.edu

Experimental Section

Materials and Methods

The commercial calcium lignosulfonates (which are derived from mason pine) were part of a by-product of sulfite pulping from Guangzhou Paper Co. Ltd., Guangzhou, China. The M_w and M_n of the original calcium lignosulfonates were 11700 and 40600, respectively. Sodium lignosulfonate and potassium lignosulfonate were prepared from the reaction of calcium lignosulfonate with sodium carbonate and potassium carbonate respectively. Methane (99.95%) was purchased from Zhuozheng Gas Co. Ltd., Guangzhou, China.

Methane Gas Hydrates Formation

To carry out the gas uptake kinetic experiments, 20.0 g of LS solution with a pre-determined concentration of LS was loaded into a high pressure stainless steel vessel with a volume of 82.0 cm^3 (Kerui Instruments Co., Gongyi, Henan, China). The temperature of the coolant was controlled by a programmable thermal circulator (DWHW-10, Kerui Instruments Co., Gongyi, Henan, China). The sample temperature in the high pressure cell was measured using a type K thermocouple (-250 to 400 ^{o}C, Tianyi Cekong Co., Henan, China). The gas pressure was monitored using a High-Accuracy Gauge Pressure Transmitter (0-20 MPa, Tianyi Cekong Co., Henan, China). Both the thermocouple and the transmitter were connected to a Digital Universal Input Panel Meter (ZNHW, Kerui Instruments Co., Gongyi, Henan, China), which communicates with a computer. Prior to each experiment, the cell was purged with methane three times to remove the air, and then pressurized to the desired pressure at the designated temperature. The temperature (T, K), pressure (P, MPa), and time (t, min) were automatically interval-logged using SuperCx 3.0 software (Kerui Instruments Co., Gongyi, Henan, China). Using this set up it was possible to obtain high resolution data (1 second between individual [T, P, t] points, 60,000 data points in a 1000 min experiment). The apparatus is shown schematically in Figure S1.

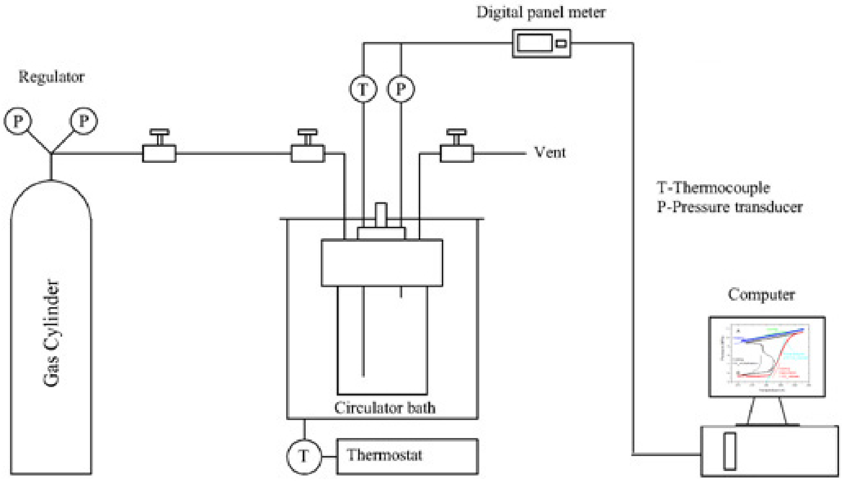

Figure S1. Schematic diagram of the experimental apparatus.

Calculation of Capacity

In this work, capacity is defined volumetrically in terms of the number of volumes of guest gas released per unit volume of hydrate material (v/v). The capacity was also calculated relative to the pressure change within the reaction vessel. The free space volume of the vessel was obtained by subtracting the sum volume of methane clathrate hydrate, unreacted water and solid LS. Taking the non-ideality factors into account, GASPAK v3.41 software (Horizon Technologies, USA) was employed to calculate the methane enclathration capacity, according to the pressure and the temperature. We assume that the liquid and gas phases inside the vessel are exclusively formed from the water and the guest gas, respectively, neglecting any dissolution of the guest gas into the liquid phase and any mixing of the water vapor in the gas phase.

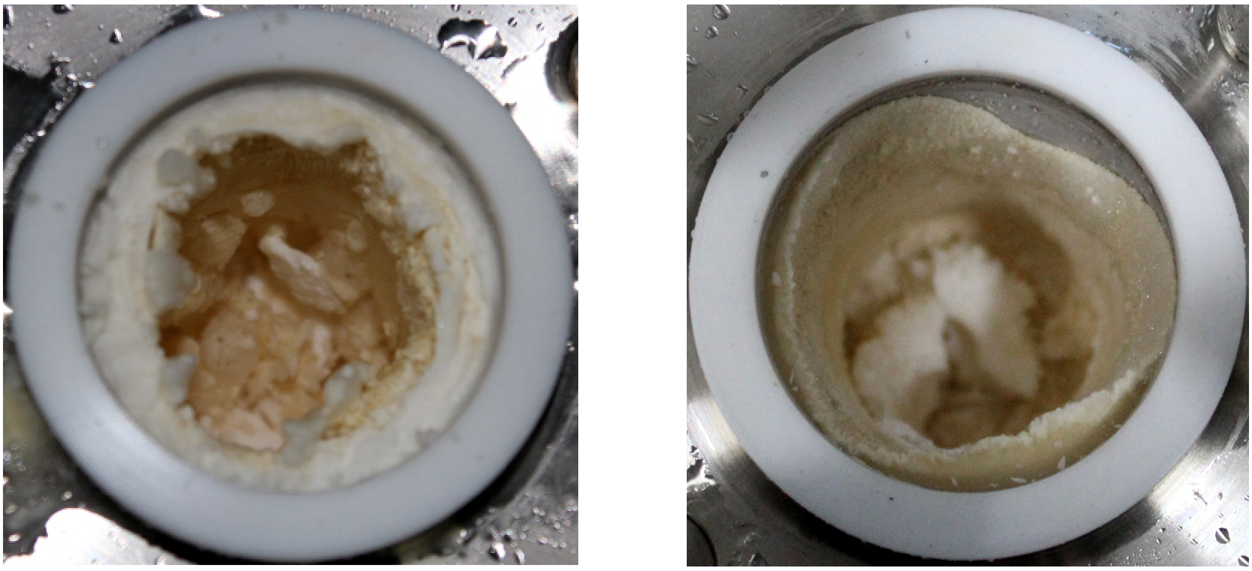

Figure S2. Methane hydrates grew upward on the vessel walls: 0.50 wt% Ca-LS (left) and 0.50 wt% Na-LS (right).