APPLIED CHEMISTRY

Toward the Efficient Production of Methane/Propane Double Hydrate

Melissa R. Prado, Yazmin Cazares, and Kenneth C. Janda*

Department of Chemistry and ISIS, University of California in Irvine, Irvine, California 92697-2025

Propane hydrate has been studied to investigate its use as a possible storage medium for methane gas. For practical purposes, hydrate formation needs to be efficient at near ambient conditions. Ice particles exposed to varying mixtures of propane and methane gas are found to form the double hydrate efficiently and may be quite effective for storing methane. For instance, exposure of the ice particles to a 2/1 methane/propane gas mixture for 18 h converts 66% of the ice to hydrate with 77% occupancy of the 5^{12} cages and a final dissociation temperature of 287 K. The samples were then decomposed to determine the pressure versus temperature at a rate of 1 K/h. It was found that deviations from equilibrium were minor. The compositions of the hydrates were determined via gas chromatography. For the 180 μm particles employed in this study, 77% of the water was converted to double hydrate over 72 h. Additional experiments were performed in which the ice particles were sequentially exposed to propane and then methane to make the double hydrate. However, this technique did not prove to be as efficient as exposure to the mixed gas. Finally, gas composition measurements during decomposition of the double hydrates reveal that the two gases are released simultaneously.

I. Introduction

Vast quantities of natural gases are stored within the lattice structures of clathrate hydrates located in deep sea sediments and in permafrost.[1,2] Because 1 m^3 of hydrate may contain as much as 180 m^3 of gas at standard temperature and pressure, hydrates act to concentrate gas.[3] So, clathrate hydrates may also serve as a storage and/or transportation medium for methane.[4] They have certain advantages over highly compressed or liquefied gas in that higher temperatures and/or lower pressures may be employed. However, formation of methane clathrates can be difficult because liquid water and methane are inherently immiscible. Of course, if clathrates are going to be used for practical applications, huge quantities must be quickly synthesized. Even on the laboratory scale, synthesis often involves pressures from 2−35 MPa at 273−288 K.[1,5] Storing methane clathrate at 273 K requires maintaining a pressure of 2.5 MPa.[1] An alternative is to employ a mixed clathrate formed with the large cavities stabilized by propane leaving the small cavities available for methane. This may allow for storage at a relatively low pressure of 0.27 MPa and a moderate temperature of 274.8 K as demonstrated by Deaton and Frost with a methane/propane double hydrate made with 63.8% propane and 36.2% methane.[6] In addition to storing methane at near ambient temperature and pressure conditions, there may be other advantages in terms of safety and environmental impact.

The experiments reported here investigate methods for quickly forming mixed methane/propane hydrates to store the maximum amount of methane at relatively low pressure and high temperature. We chose to investigate the methane/propane mixed hydrates because propane is readily available and forms sII hydrate that can, in principle, store two methane molecules for every propane molecule. The sII hydrate contains two 5^{12} cages (dodecahedra formed from 20 water molecules with an oxygen atom at each vertex and a diameter of 5.02 Å) for every $5^{12}6^4$ cage (formed from 28 water molecules with a diameter of 6.6

Å). The smaller cages nearly match the methane diameter, 4.36 Å, while the larger cages nearly match the propane diameter, 6.28 Å. Nearly full occupancy of the cages results in a very stable hydrate with a melting point, or dissociation temperature, of nearly 284 K at a pressure of 1 MPa for a double hydrate formed from a 2/1 methane/propane mixture (see below).

Phase equilibrium on propane + methane hydrate was first studied by Deaton and Frost in 1946[7] and subsequent studies on the binary hydrate were performed for various gas compositions of methane and propane.[8−11] In 1988, cross-polarization/ magic angle spinning ^{13}C NMR techniques confirmed that the cage-dependent ^{13}C chemical shift of enclathrated methane can be used to determine the relative cage occupancies by methane.[12] Further important work was published in 2002, which dealt with the use of additives to form a C_3H_8 hydrate at lower pressures and higher temperatures. Addition of methane molecules to the C_3H_8 hydrate system resulted in shifting the hydrate equilibrium toward lower pressures and higher temperatures, confirming that methane serves to stabilize the propane hydrate.[13] Growth rates of methane/propane hydrate were reported in 2004, where mixed hydrates were prepared by condensing the gases on powdered ice and characterized by ^{13}C NMR spectroscopy. Initial growth rates were rapid, followed by a slower rate of hydrate formation.[14] Kumar et al.[15] found the formation rate of methane− propane−water to hydrate to range from 0.0010 to 0.0025 mol/ min.

In the present study, the efficient production and incorporation of methane into the propane hydrate sII is investigated. As it is well-known,[14−17] complete conversion of ice to propane clathrate is time-consuming. Therefore, several methods were investigated to produce the hydrate more rapidly and to optimize the storage of methane. Both sequential and simultaneous addition of the gases to finely divided ice particles at different pressures were investigated. After samples were formed and decomposed, the gases were analyzed by gas chromatography to determine the occupancy ratios and percent conversion of the ice particles to hydrate. For propane hydrate, a Clausius− Clapeyron plot was made from temperature and pressure

* To whom correspondence should be addressed. E-mail: (M.R.P.) melissap@uci.edu, (K.C.J.) kcjanda@uci.edu.
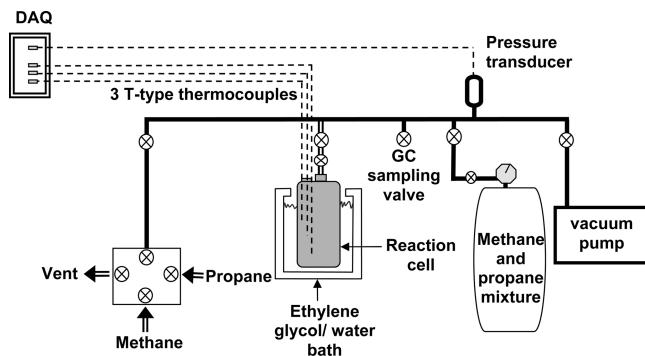
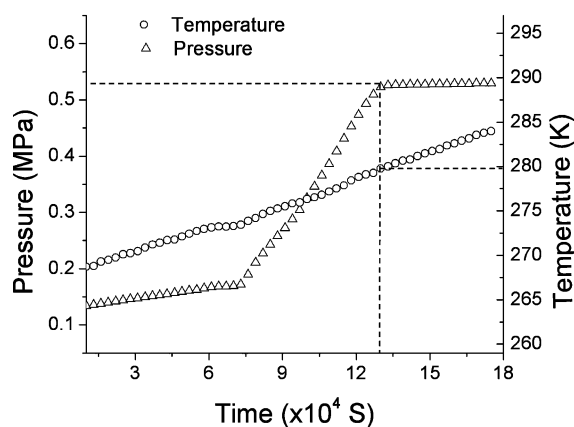**Figure 1.** Schematic of the experimental apparatus.

Figure 2. Temperature and pressure during decomposition of propane hydrate. The decomposition is not complete until $T = 280$ K is reached. This is close to the thermodynamic melting point. The points where the dashed lines intersect on the pressure and temperature graphs will be referred to as the highest decomposition pressure and highest decomposition temperature, respectively, for this sample.

measurements to determine whether equilibrium was maintained during decomposition of the hydrate.

II. Experimental Section

Our goal was to work with large enough samples to provide insight into large scale synthesis but small enough so that gas waste was minimized. Therefore, we studied 30 g ice samples, and the apparatus was constructed to conveniently process several samples per week.

A. Experimental Apparatus. The schematic diagram of the apparatus constructed for this study is displayed in Figure 1. A stainless steel manifold line was employed to connect the reaction cell to gas supply lines, the vacuum pump, vent, and gas chromatograph sampling valve. The reaction cell is a cylindrical stainless steel cell (7.62 cm in diameter, effective volume of 310 cm^3) fabricated in the UC Irvine machine shop. The stainless steel cell contains 3 T-type thermocouples (Omega Engineering, part: TJC36-CPSS-040U-12-SMP-M, 73−623 K ± 1.0 K) placed at varying heights within the cell. The cell was immersed in a temperature controlled ethylene glycol/water bath to maintain stable temperature conditions. A pressure transducer (Omega Engineering, model: PX303−1KG5V, 0−1000 psig ± 0.25% full scale) was attached to the manifold line to monitor pressure. The gases were introduced to the reaction cell via the manifold line and controlled by pressure regulators. A sampling valve was attached directly to the manifold line, wherefrom gas compositions were determined by an off-line gas chromatograph (GC; Shimadzu model GC-1014). The gas

chromatograph was calibrated against methane/propane mixtures prepared on the gas manifold, and so, the precision of the gas composition measurements is that of the pressure transducer.

B. Materials and Preparation. Research grade methane (99.999%) and chemically pure grade propane (99.0%) supplied from Airgas were used in preparing the gas hydrates. The gas mixtures were prepared by adding the two gases to a third tank and allowing them to mix for 24 h.

C. Experimental Procedure. Mixed methane/propane samples were prepared in two different ways for this study. First, propane hydrate was prepared and then exposed to methane. Second, the gases were mixed in advance and added together. We also performed studies on pure propane hydrate for comparison.

Following the suggestion of Stern et al.,[5,18] powdered ice was used as a starting material in order to maximize the surface area of ice exposed to gas. The powdered ice was made by grinding small ice pellets into a fine powder. The ice pellets were formed by a steady drip of nanopure water from a buret into liquid nitrogen. The ice pellets were then strained from the liquid nitrogen and ground in a coffee grinder (Cuisinart model: DBM-8) at 253 K. The powder was then forced through a 180 μm sieve. Powdered ice (30 g) was placed in a reaction cell precooled with liquid nitrogen. The cell was then sealed, placed in a water bath preset to 269 K, and attached to the manifold line, where the head space of the cell was evacuated to eliminate air.

For the studies for which propane hydrate was first prepared and then exposed to methane, propane was introduced to the reaction cell at a rate of 0.2 MPa/h (to minimize melting of the fine powder) to a total pressure of 0.38 MPa. This pressure was chosen to avoid forming liquid propane. The temperature of the sample was increased to 272 K, and the sample remained exposed to propane for a period of 72 h. Next, methane was added to the desired final pressure. After 24 h, the samples were placed in a freezer set to 243 K. After 24 h, analysis of the hydrate was performed by connecting the sample back to the manifold line, adjusting the temperature to 253 K, evacuating the gas above the hydrate, and then heating to release gas from the hydrate while recording the temperature and pressure. Periodic samples of 100 μL were collected for analysis by gas chromatography during decomposition of the hydrate. To obtain the amount of gas consumed and subsequently the amount of ice converted to hydrate, eq 1 was used:

$$n = PV/ZRT \tag{1}$$

where P, V, and T are the gas pressure, volume, and temperature, respectively. R is the gas constant, and Z is the compressibility factor obtained from the Peng−Robinson equation of state.[19]

When using premixed methane/propane gas, the procedure was quite similar. In this case, several different hydrate formation procedures were employed to try to maximize gas uptake, and these will be described more completely below.

III. Results and Discussion

Our goal in carrying out the experiments was to increase the rate of formation of mixed methane/propane clathrate hydrate. In addition, we carried out a Clausius−Clapeyron analysis of the pressure versus temperature curve for propane hydrate and compared the resulting ΔH values to those in the literature.[20]

A. Propane Hydrate. First, a pure propane hydrate sample was studied to provide a reference for the mixed gas studies. The propane hydrate was formed by placing 30 g of powdered ice in a precooled reaction cell, the headspace was evacuated to eliminate air, and propane was introduced to the reaction cell at a rate of 0.2
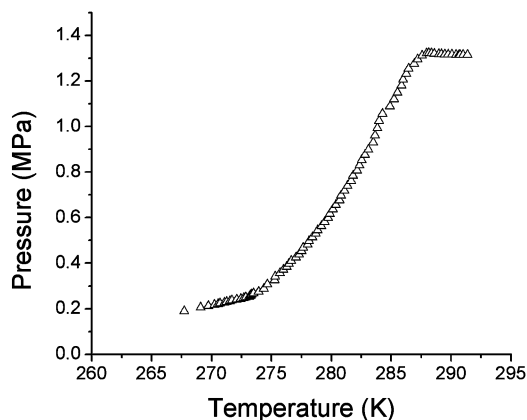
Figure 3. Plot of pressure vs temperature during decomposition of a methane/propane double hydrate formed over 72 h with a 2:1 methane/propane mixture at 1.1 MPa and 272 K. Note that if one wanted to store the double hydrate at 1.0 MPa, the temperature could be maintained at 283 K.

Figure 4. Total pressure and ratio of methane/propane molecules as a function of temperature for the sequentially formed propane hydrate pressurized with 1.48 MPa of methane for 24 h.

MPa/h to a total pressure of 0.38 MPa at 272 K. After each sample was formed, it was decomposed by raising the temperature at a rate of 0.36 deg/h. A typical data set for pressure and temperature versus time is shown in Figure 2. Note that the sample temperature stalls slightly at 273 K indicating that some of the water is still in the form of ice. Also, note that the rate of pressure increase changes when the sample reaches 273 K. This is due to the fact that ΔH for hydrate decomposition depends on whether it decomposes to solid or liquid water. Applying the Clausius−Clapeyron relation to the data above and below 273 K yields values of 129 and 26 kJ/mol, respectively for ΔH. These compare to the values reported by Handa et al.,[21] 129.2 and 27 kJ/mol, respectively, so we were not too far from maintaining equilibrium. In this sense, the hydrate shows little of the metastability that has been reported for methane hydrate.[5]

We conclude that over the time scale of these decomposition experiments, equilibrium was maintained. The pressure leveled off at 0.53 MPa at 280 K, again, close to the equilibrium dissociation temperature for that pressure. From the total gas release, it was determined that 81% of the initial 180 μm ice powder had been converted to propane hydrate by this synthesis procedure. To investigate the effect of particle size, a similar experiment was performed in which the ice was sieved through a 106 μm mesh before loading into the cell. Propane hydrate yield increased to 91%. Clearly, to optimize hydrate synthesis, one would like to employ the finest possible mesh. However, using the smaller mesh is much more time-consuming, and the 180 μm mesh was employed in the subsequent experiments.

B. Hydrate from Premixed Methane/Propane Gas. Because our goal is to store propane and methane as efficiently as possible, and since the ratio of small to large cages is 2:1, we first studied a 2:1 methane to propane ratio for the synthesis gas. The powdered ice was exposed to 1.1 MPa of the gas mixture for 6, 18, and 72 h, and then the samples were slowly decomposed while monitoring pressure and temperature as described above.
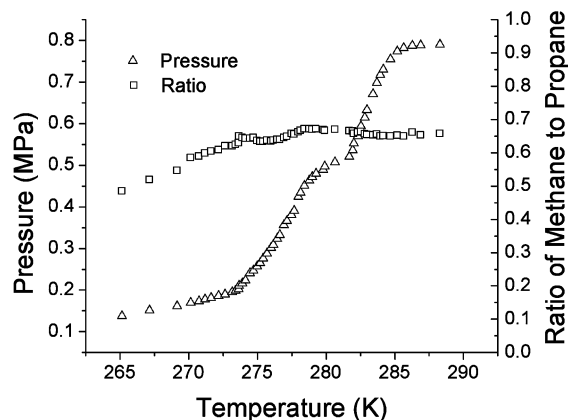
Figure 3 shows the pressure as a function of temperature during decomposition of the methane/propane double hydrate formed over 72 h using the 2:1 sample mixture and heated from 253 K at a rate of 1 K/h. As for pure propane hydrate, there are two regions of pressure increase: above and below the water melting point. Decomposition was complete by 287 K, yielding a final pressure of 1.3 MPa. Analysis by gas chromatography shows that this gas was 58% methane and 42% propane. So, more than 50% of the available small cages were filled with methane even though the sample was prepared with a modest initial pressure.

Because the methane partial pressure maintained in this study is well below that necessary to obtain pure methane clathrate, we assume that the percent conversion of ice to clathrate is roughly given by the amount of propane that is trapped. This analysis yielded a conversion fraction of 77 ± 5% for two samples synthesized with the 2:1 methane/propane mixture at 1.1 MPa. More importantly, the data shows that significant amounts of methane were incorporated into the clathrate during formation: 70 ± 1% of the available 5^{12} cages were occupied by methane. Note that some of the sample decomposed as the head gas was evacuated before the decomposition study. So, the percent conversion is slightly higher than 77%. Table 1 reports similar data for these runs and those for a 2.8:1 methane/propane mixture, also with total initial pressure 1.1 MPa, and for sample preparation times ranging from 6 to 18 h.

The data in Table 1 shows that, for the 2:1 methane/propane mixture, increased exposure of the ice particles to the gas continues to improve the percent conversion up to 72 h. Most probably, the hydrate that is formed initially serves to isolate the remaining ice from the gas. So, for a practical process, one would need to employ either smaller initial particle sizes or some method to continuously expose the remaining ice surface to the gas. The methane/propane ratio in the solid decreases very slightly with increased exposure time. For the mixture with the 2.8:1 methane to propane ratio, there was slightly more methane uptake into the available small cages, but fewer small cages were formed due to the

Table 1. Properties Observed for Double Hydrates Formed from Two Different Mixtures for Different Synthesis Times

time that ice was exposed to gas (h)	initial gas composition of methane/propane	final decomposition pressure (MPa)	final decomposition temperature (K)	final hydrate gas composition: methane/propane	% of ice converted to hydrate	% of 5^{12} cages filled with methane
6	2/1	1.00	287	1.50	57	75
18	2/1	1.15	287	1.54	66	77
72	2/1	1.27 ± 0.06	289 ± 0.7	1.41 ± 0.01	77 ± 5	70 ± 0.7
6	2.8/1	0.882	286	1.61	48	80
18	2.8/1	0.799	285	1.54	45	77

Table 2. The Highest Decomposition Temperature and Pressure Released During Decomposition of Sequentially Formed Double Hydrates

methane partial pressure (MPa)	final decomposition pressure (MPa)	final decomposition temperature (K)	final hydrate gas composition: methane/propane	% of ice converted to hydrate	% of 5^{12} cages filled with methane
0.38	0.793 ± 0.2	284 ± 2	0.508	79	26
0.66	0.905 ± 0.1	287 ± 5	0.671	80	34
1.07	0.851 ± 0.1	284 ± 3	0.654	77	33
1.48	0.927 ± 0.06	287 ± 4	0.671	82	34

lower partial pressure of propane. The partial pressure of propane in this case was 0.3 MPa, still well above the propane hydrate vapor pressure. In terms of gas storage at near ambient conditions, the data in Table 1 indicates that solid hydrate can be maintained at temperatures up to 285 K with modest total pressures in the range of 1 MPa. Alternatively, if lower pressures are preferred, the hydrate can be maintained at 0.2 MPa for temperatures slightly below 273 K.

C. Sequential Methane/Propane Hydrate Production. As an alternate to simultaneous mixed gas clathrate production, we investigated the sequential storage of methane after propane hydrate was first produced. This study was motivated by the possibility that a stable propane hydrate might absorb and release methane reversibly. Propane hydrate was formed as described above and then exposed to varying pressures of methane gas for 24 h. In addition to measuring the pressure release as a function of temperature, gas chromatographic analysis was performed during decomposition to determine whether the methane is released preferentially at temperatures below the final decomposition temperature. Figure 4 shows an example of such data. In this case, the propane hydrate was exposed to methane at a partial pressure of 1.48 MPa for 24 h. The pressure versus temperature plot of the sample formed by this procedure is quite similar to that formed by the mixed gas discussed above, except that the final pressure is lower. The lower final pressure shows that sequential exposure to methane is less efficient than synthesis with premixed gases. However, in spite of obtaining lower final pressures, the sequentially formed hydrates are still capable of filling 33% of the theoretically available 5^{12} cages. The methane to propane ratio in the gas phase is nearly constant over the decomposition range. From this, we conclude that the methane that was absorbed was distributed relatively evenly over the surface of the particles.

Table 2 summarizes the results from the decomposition of gas hydrate samples synthesized by exposure of propane hydrate to four different methane pressures, ranging from 0.38 to 1.48 MPa. The amount of methane trapped by the propane hydrate increased only slowly as the methane pressure was raised. The final gas composition for the sequentially formed propane hydrate pressurized with 1.48 MPa of methane was 60% propane and 40% methane. 82% of the ice was successfully converted to hydrate, and 34% of the 5^{12} cages was occupied by methane. The cage occupancy of methane molecules in the small cages remained roughly constant throughout decomposition of the hydrate, indicating that both the small and large cages of the sII breakdown at the same rate during decomposition. This was true for all sequentially formed methane/propane hydrates. This indicates that, for the decomposition rates of these experiments, near equilibrium conditions were maintained.

If the initial particle size were small enough, perhaps the sequential dosing technique might be comparable in efficiency to the dosing with mixed gas. However, it appears that there is no advantage to using the sequential dosing in terms of selective release of methane upon warming for the decomposition rates employed in this study.

IV. Conclusions

The goals of this study were to determine the efficiency of forming methane/propane double hydrate by exposing small ice particles to gas mixtures and to determine if the resulting hydrates decompose close to equilibrium conditions for a given rate of temperature increase. We find that ice particles screened through a 180 μm mesh yield 81% propane hydrate when exposed to 0.38 MPa propane for 72 h. Propane hydrate synthesis was more efficient for small particle sizes, but the time to create the particles increased significantly, and we employed the 180 μm mesh in the mixed gas studies reported here. Decomposition of the propane hydrate prepared by this technique yielded ΔH values in reasonable agreement with the literature. This indicates near-equilibrium conditions were maintained during decomposition.

It was found that direct exposure of the ice particles to a methane/propane mixture was more efficient for forming the methane/propane double hydrate than was exposure of propane hydrate to pure methane gas. For the 2:1 methane/propane mixture at 1.1 MPa, 57% of the ice was converted to double hydrate in 6 h, increasing to 77% in 72 h, as measured by propane uptake. Also, about 70% of the available 5^{12} cages were filled by methane at the end of the run. In the literature, it is common to compare the methane and propane density in the hydrate to an effective ideal gas pressure. In the case of the best sample produced here, the effective gas pressures are 5.4 MPa for propane and 7.6 MPa for methane. The resulting hydrate decomposed near equilibrium conditions for a temperature ramp of 1 K/h. At 270 K, the mixed propane/methane vapor pressure of the sample was 0.2 MPa, and the vapor pressure gradually increased to 1.25 MPa at 289 K. So, the double hydrate prepared by these techniques can store significant amounts of methane under mild conditions of temperature and pressure.

Literature Cited

(1) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(2) Kvenvolden, K. A. Methane Hydrate a Major Reservoir of Carbon in the Shallow Geosphere. *Chem. Geol.* **1988**, *71*, 41.

(3) Sloan, E. D. Gas Hydrates: Review of Physical/Chemical Properties. *Energy Fuels* **1998**, *12* (2), 191–196.

(4) Koh, C. A. Towards a Fundamental Understanding of Natural Gas Hydrates. *Chem. Soc. Rev.* **2002**, *31*, 157.

(5) Stern, L. A.; Kirby, S. H.; Durham, W. B. Peculiarities of Methane Clathrate Hydrate Formation and Solid-State Deformation, Including Possible Superheating of Water Ice. *Science* **1996**, *273* (5283), 1843.

(6) Deaton, W. M.; Frost, E. M., Jr., Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipe Lines, U.S. Bureau of Mines Monograph 8, July 1946; p 101.

(7) Deaton, W. M.; Frost, E. M., Jr. *Oil Gas J.* **1937**, *36* (1), 75.

(8) McLeod, H. O.; Campbell, J. M. Natural Gas Hydrates at Pressures to 10,000 psia. *J. Petrol. Tech.* **1961**, *222*, 590.

(9) Verma, V. K.; Hand, J. H.; Katz, D. L. Gas Hydrates from Liquid Hydrocarbons (Methane-Propane-Water System; AlChE-VTG Joint Meeting, Munich, Germany, 1974; p 10.

(10) Song, K. Y.; Kobayashi, R. Measurement and Interpretation of the Water Content of a Methane-Propane Mixture in the Gaseous State in Equilibrium with Hydrate. *Ind. Eng. Chem. Fundam.* **1982**, *21* (4), 391.

(11) Thakore, J. L.; Holder, G. D. Solid Vapor Azeotropes in Hydrate-Forming Systems. *Ind. Eng. Chem. Res.* **1987**, *26* (3), 462.

(12) Ripmeester, J. A.; Ratcliffe, C. I. Low-Temperature Cross-Polarization/Magic Angle Spinning Carbon-13 NMR of Solid Methane Hydrates: Structure, Cage Occupancy, and Hydration Number. *J. Phys. Chem.* **1988**, *92* (2), 337.

(13) Mooijer, M. M.; Peters, C. J.; De Swaan Aarons, J. Gas Hydrate Phase Equilibria for Propane in the Presence of Additive Components. *Fluid Phase Equilib.* **2002**, *193*, 245.

(14) Kini, R. A.; Dec, S. F.; Sloan, E. D., Jr. Methane + Propane Structure II Hydrate Formation Kinetics. *J. Phys. Chem. A* **2004**, *108*, 9550.

(15) Kumar, R.; Linga, P.; Moudrakovski, I.; Ripmeester, J.; Englezos, P. Structure and Kinetics of Gas Hydrates from Methane/Ethane/Propane Mixtures Relevent to the Design of Natural Gas Hydrate Storage and Transport Facilities. *AIChE J.* **2008**, *54*, 8.

(16) Giavarini, C.; Maccioni, F.; Santarelli, M. L. Formation Kinetics of Propane Hydrates. *Ind. Eng. Chem. Res.* **2003**, *42* (7), 1517.

(17) Englezos, P. Clathrate Hydrates. *Ind. Eng. Chem. Res.* **1993**, *32* (7), 1251.

(18) Stern, L. A.; Circone, S.; Kirby, S. Proceedings of the 5th International Conference on Gas Hydrates, June 2005, Norway Paper 1046.

(19) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(20) Sloan, E. D.; Fleyfel, F. Hydrate Dissociation Enthalpy and Guest Size. *Fluid Phase Equilib.* **1992**, *76*, 123.

(21) Handa, Y. P. Compositions, Enthalpies of Dissociation, and Heat Capacities in the Range 85 to 270 K for Clathrate Hydrates of CH_4, C_2H_6, C_3H_8. *J. Chem. Thermo.* **1986**, *18*, 15.