Measurements of Equilibrium Pressures and Temperatures for Propane Hydrate in Silica Gels with Different Pore-Size Distributions

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Equilibrium pressures for the dissociation of propane hydrate confined in silica gel pores of nominal radii 7.5, 5.0, 3.0, and, 2.0 nm were measured across a wide temperature range, and were higher than those for bulk propane hydrate. The upward shift from the bulk pressures, which depended on the pore size, was 200−300% for the smallest pore size. In each of the pressure−temperature profiles, the temperature at which the four phases (hydrate, ice, liquid water, and gas) apparently coexisted was identified, and this temperature was a linear function of the reciprocal pore size. The enthalpy of dissociation for the equilibrium involving hydrate, liquid water, and gas was estimated from the data. The change with pore size in this apparent enthalpy appeared to be analogous to the variation in the heat of melting of pore ice as sometimes reported.

Introduction

Low-molecular-weight gases, such as carbon dioxide, hydrogen sulfide, and sulfur dioxide, and some other gases including nitrogen and light hydrocarbons, react with water at high pressures and ordinary temperatures (or at moderate pressures and low temperatures) to form gas hydrates. Gas hydrates are crystalline icelike clathrates in which each water molecule is hydrogen bonded to its nearest neighbors, forming a cagelike structure in which the gas molecules are occluded. The structure type and composition of hydrates has been investigated using analytical techniques including solid-state nmr[1] and Raman[2] spectroscopy. Work on gas hydrates in porous media was of academic interest until the recent discovery of natural gas hydrate deposits in Canadian[3] and Russian[4] permafrost and in subseafloor deposits in outer continental shelves.[5] It is estimated that the volume of natural gas in these deposits is enormous, representing large potential sources of a clean fuel. The eventual production of natural gas from these reservoirs is of great interest to both the private and public sectors.

To understand the conditions at which gas hydrates form or dissociate in gas reservoirs, the synthesis and decomposition of gas hydrates in porous media should be investigated. Makogon[6] studied the formation of methane hydrate in sandstones of different pore sizes. His study with pore radii of 5.7, 5.0, and 3.5 μm suggested that the pressure required for hydrate formation increased as the pore size was decreased. The equilibrium pressure for the dissociation of hydrates and the thermodynamic properties in large pores are apparently nearly identical with those in the bulk.[7] To understand in detail the effects of pores on the formation and dissociation characteristics of hydrates, one needs to conduct experiments in much smaller pores. Differences in chemical potentials and interfacial forces between the bulk and pore water affect hydrate formation in

such pores. In addition, many porous materials have broad pore size distributions that also affect the formation and the dissociation characteristics of the hydrate. Therefore, the study of hydrate formation/dissociation in porous media is much more complex than that in the bulk. Handa and Stupin[8] have studied methane and propane hydrates in silica gel of 7.5 nm nominal pore radius, and Uchida et al.[9] have investigated the properties of methane hydrate in three porous Vycor glass samples with pore radii of 25, 15, and 5 nm. In addition, Henry et al.[10] and Clarke et al.[11] have proposed interpretations of the data of Handa and Stupin[8] based on the addition of a capillary pressure term to the statistical-thermodynamic model of van der Waals and Platteeuw.[12] The inability of these interpretations (see Figure 5 of ref 10 and Figure 4 of ref 11) to adequately reproduce the experimental equilibrium pressures of Handa and Stupin could be due to either or both of two sources. First, it has yet to be shown that all of the effects of the small pore size on the equilibrium have been accounted for correctly. Second, as suggested by the authors of previous work,[10,11] the discrepancy may be due to the assumption in the model that a single pore size can adequately represent the sample, which in reality involves a rather broad distribution of pore sizes.[13] To provide more experimental data for use in future modeling efforts, and to gain a better understanding of this complex system, we have performed experiments and investigated the properties of propane hydrates in four silica gel samples with nominal pore radii of 2, 3, 5, and 7.5 nm, respectively. Such data for a range of pore sizes, all of which involve capillary effects that strongly affect the equilibrium pressure, should help to delineate the effects of pore size on hydrate dissociation. In addition, they should provide enough experimental data for validation of any future model capable of explaining the discrepancy between the experimental data and previous models reported in the literature.

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Experimental Methods

Propane with minimum purity of 99.5 mol % was obtained from Matheson. Nitrogen desorption and adsorption studies using Quantachrome Corp Autosorb-1 equipment were used to

TABLE 1: Physical Properties of Silica Gel Samples

silica gel	SG75A	SG75B	SG50	SG30	SG20
nominal pore radius (nm)	7.5	7.5	5.0	3.0	2.0
particle size (μm)	33−74	74−250	63−210	33−74	193−595
average pore volume (cm^3/g) Autosorb-1	1.144	1.147	1.021	0.82	0.638
vendor data	1.15	NA	0.92−1.2	0.75	0.68
sorbed water	1.112	1.140	1.050	0.768	0.600

determine the pore size distribution[14] and pore volume of each of the silica gel samples used in the experiments.

A high-pressure cell about 30 mL in volume was constructed using stainless steel tubing of 1 in. outside diameter (o.d.) (0.091 in. wall thickness) and 1 in. to 0.25 in. Swagelock reducers. One of the reducers was fitted with 0.125 in. tubing and a Swagelock fitting to connect a transducer to the cell. The silica gel samples, without any further treatment, were placed in a desiccator containing degassed, distilled water for 4 to 6 days to prepare silica gel with sorbed water. The cell was loaded with about 140 5-mm-diameter glass beads, and a slurry consisting of liquid nitrogen and silica gel containing pore water was poured over the glass beads, coating them with the silica gel. The sealed cell was then connected to a vacuum manifold and cooled in liquid nitrogen. The cell was evacuated to about 50 milliTorr, and held at that pressure for 30 min to remove air from the cell. The cell was transferred to a temperature-controlled chiller (Neslab model RTE 140), and then connected to the propane cylinder and the transducer. The bath temperature was read with a Hart Scientific model 1006 MicroTherm thermometer with a sensitivity of 0.001 K. The bath temperature was stable to within ±0.4%. The pressure measurements were made with a 1.36-MPa full-scale transducer (Rosemount model 1511), which was calibrated by the dead-weight method. The accuracy of the transducer was 0.11% of full scale. The preparation of the hydrates and the subsequent determination of the equilibrium pressure−temperature profiles for their dissociation were performed in a manner similar to that used previously by Handa and Stupin[8] for a silica gel with nominal 7.5-nm pores. In the present work, two different sources were used for the silica gel with a nominal pore radius of 7.5 nm, one consisting of particles having a size range of 33−74 μm (Davisil), and the other (Baker) 74−250 μm. In this work we report equilibrium pressure−temperature data for the dissociation of propane hydrates in silica gels with nominal pore radii of 2.0, 3.0, 5.0, and 7.5 nm.

Results and Discussion

Silica Gel Properties. The physical properties of silica gels (identified as SG75A, SG75B, SG50, SG30, and SG20) having four different nominal pore radii are listed in Table 1. The surface areas for the silica gel samples, determined by Auto-sorb-1 were 294.6 m^2/g, 259.7 m^2/g, 287.4 m^2/g, 459.2 m^2/g, and 585.2 m^2/g for SG75A, SG75B, SG50, SG30, and SG20, respectively. The pore size distributions were found by applying the method described in ref 14 to the Autosorb-1 data. The distribution found for SG75A is shown in Figure 1. The distribution curve is nearly symmetrical, with a mean pore radius of 7.5 nm and a half-width of 4.0 nm. The distributions for SG75B and SG50 were similar to that for SG75A, whereas those for the other silica gel samples were multimodal, probably because of experimental uncertainties in the measurements. The water uptake for each of the silica gels is given in Table 1. These uptakes are consistent with the pore volumes given by the manufacturer and those measured by Autosorb-1.

Propane Hydrate Properties. The equilibrium pressures obtained for the dissociation of propane hydrate in silica gel
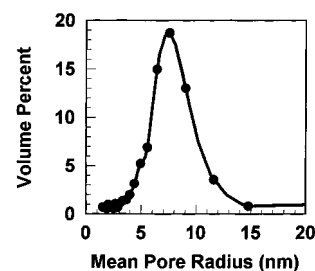

Figure 1. Volume percent as a function of mean pore radius for nominal 7.5 nm silica gel pores based on the Autosorb-1 desorption isotherm.
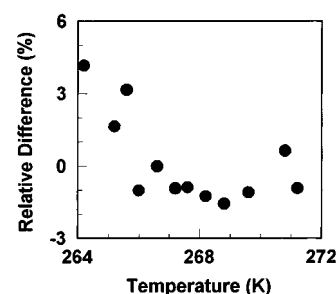

Figure 2. Percent relative differences between the equilibrium pressures reported in this work for propane hydrate formation in silica gels with a 7.5 nm nominal pore radius and those by Handa and Stupin.[8]
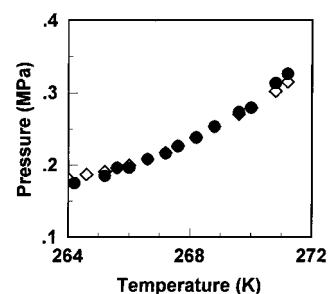

Figure 3. Experimental equilibrium pressures for propane hydrate formation in silica gels with a 7.5 nm nominal pore radius for particles in the size range 33−74 μm (●) and 74−250 μm (◇).

with nominal 7.5 nm radius pores (SG75A) were in excellent agreement with the results published by Handa and Stupin,[8] and the percent relative differences between the two are shown in Figure 2. The deviations between the results of these two investigations, except for three observations, were 0.1−1.7%. Equilibrium pressure−temperature data for the silica gel samples having nominal pore radii of 7.5 nm, but with widely differing particle sizes are shown in Figure 3. The results of these two experiments are in good agreement, indicating that the dissociation of these hydrates was controlled primarily by the pore radius, not the particle size. This supports the conclusion that the hydrate formed in the silica gel pores, and not in the interparticle spaces.

The equilibrium pressure−temperature data for the silica gel samples (corrected for the vapor pressure of water) are given in Table 2, and those for SG75A, SG50, SG30, and SG20 are shown graphically in Figure 4. Included in the figure are the

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TABLE 2: Equilibrium Pressure−Temperature Data for Propane Hydrate in Silica Gel Pores of Various Nominal Radii

| 7.5 nm			5.0 nm		3.0 nm		2.0 nm	
T (K)	P (Mpa)[a]	P (Mpa)[b]	T (K)	P (Mpa)	T (K)	P (Mpa)	T (K)	P (Mpa)
264.2	0.175	0.181	263.0	0.201	253.0	0.160	246.0	0.190
265.2	0.185	0.191	263.5	0.208	254.0	0.165	246.5	0.194
265.6	0.195	0.196	264.0	0.215	255.0	0.171	247.0	0.197
266.0	0.196	0.200	264.5	0.221	256.0	0.175	247.5	0.202
266.6	0.208	0.208	265.0	0.231	257.0	0.181	248.0	0.205
267.2	0.215	0.217	265.5	0.234	258.0	0.186	248.5	0.208
267.6	0.226	0.226	266.0	0.241	259.0	0.196	249.0	0.212
268.2	0.237	0.238	266.5	0.250	260.0	0.204	249.5	0.217
268.8	0.252	0.253	267.0	0.260	261.0	0.215	250.0	0.220
269.6	0.273	0.270	267.5	0.270	262.0	0.226	250.5	0.224
270.0	0.278	0.279	268.0	0.283	263.0	0.238	251.0	0.228
270.8	0.313	0.302	268.5	0.294	264.0	0.251	251.5	0.232
271.2	0.326	0.315	269.0	0.306	265.0	0.264	252.0	0.237
			269.5	0.319	266.0	0.273	252.5	0.240
					267.0	0.280	253.0	0.244
					268.0	0.287	253.5	0.250
							254.0	0.255
							254.5	0.260
							255.0	0.265
							255.5	0.270
							256.0	0.275
							256.5	0.279

[a] Silica gel SG75A. [b] Silica gel SG75B.
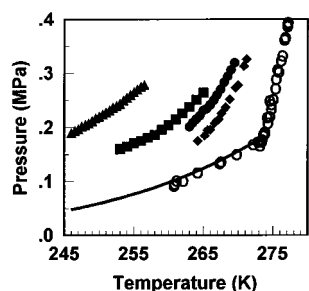
Figure 4. Experimentally measured equilibrium pressures in silica gels of nominal pore radii 2 (▲), 3 (■), 5 (●), and 7.5 (◆) nm. Also shown are results for bulk hydrate formation (○) and hydrate formation in sand (solid curve).

experimentally measured data for bulk propane hydrate,[15] and for the dissociation of this hydrate in sand.[7] The data in sand are used for comparison purposes over the temperature range where there are no data available for the bulk. Figure 4 shows that there is close correspondence in the region where the bulk values and those for hydrate formation in sand (calculated from the empirical equation given by Kamath[7] from fits to experimental data) overlap. Figure 4 shows that the relative increase in the dissociation pressures reported in this work for pore hydrate as compared with that for bulk hydrate varied with the pore size. The increase was 53−87% for the nominal 7.5 nm pores, 79−110% for the nominal 5 nm pores, 78−131% for the nominal 3 nm pores, and 200−300% for the nominal 2 nm pores.

Plots of ln(f/MPa) as a function of reciprocal temperature are shown in Figure 5, where the pressures from Table 2 have been converted to fugacities using the empirical equation for the second virial coefficient given by Pitzer and Curl.[16] Also shown in the figure are linear fits to the function

$$\ln(f/\text{MPa}) = A + 1000B/T \qquad (1)$$

The best fits of eq 1 for the equilibrium involving hydrate, ice, and gas (hig) below the apparent quadruple point, and for the equilibrium between hydrate, liquid water, and gas (hlg) above the apparent quadruple point, are listed in Table 3 for the four
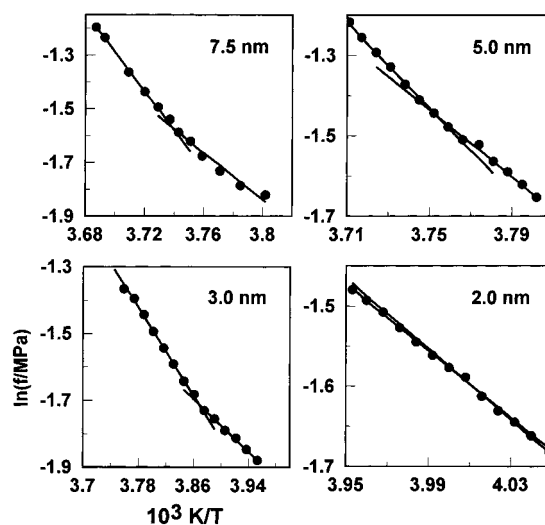

Figure 5. Equilibrium fugacities of propane hydrates in silica gels of nominal pore radii 2, 3, 5, and 7.5 nm plotted against reciprocal temperature. Also shown are fits to the data using eq 1 (solid lines).

TABLE 3: Parameters Used in Eq 1 to Generate the Linear Fits Shown in Figure 5

nominal pore radius (nm)	A	B (K)	proposed equilibrium type[a]
7.5	14.8190	−4.3836	hig
	25.6232	−7.2787	hlg
5.0	14.2165	−4.1736	hig
	18.4615	−5.3043	hlg
3.0	5.9160	−1.9719	hig
	11.0265	−3.2930	hlg
2.0	7.2235	−2.1996	hig
	6.7550	−2.0828	hlg

[a] g, gas; h, hydrate; i, ice; l, liquid water.

nominal pore sizes considered in this work. In arriving at these fits, we divided each data set into two parts, and linear fits were determined for each region. We then varied where the data were divided to obtain the fits that maximized the R^2 value for each region. The point of intersection of the two lines obtained in
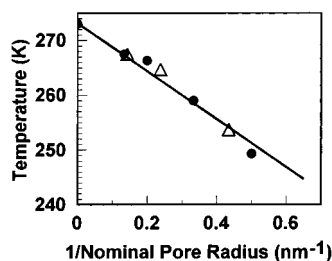
Figure 6. Apparent quadruple point temperatures (●) for propane hydrate as a function of the reciprocal of the nominal pore radius. The quadruple point temperature for the bulk occurs as $1/r \rightarrow 0$ nm^{-1}. Also shown are the theoretical melting point temperature for pore water obtained from eq 2 (solid line), and experimental melting points of water in pores (△) estimated by Handa et al.[13]

this manner for each set of data gave the temperature and pressure at which hydrate, ice, liquid water, and gas apparently coexisted (the quadruple point). The apparent quadruple point temperatures were 267.1, 266.38, 259.0, and 249.39 K for the nominal 7.5, 5.0, 3.0, and 2.0 nm pores, respectively. The apparent quadruple point for the nominal 7.5 nm pores was in good agreement with the melting point of ice (267.5 K) in this size pore determined calorimetrically by Handa and co-workers.[13] The melting point of ice in pores can be estimated using[17]

$$T_m^{\text{pore}} = T_m^{\text{bulk}}\left[1 - \frac{2\sigma_{\text{iw}}}{\rho_w \Delta H_{\text{fw}} r_b}\right] \qquad (2)$$

In eq 2, T_m^{bulk} is the bulk melting temperature (273.15 K), σ_{iw} is the surface tension between water and ice (0.0267 J/m^2), ρ_w is the specific density of water (1000 kg/ m^3), ΔH_{fw} is the specific enthalpy of fusion of bulk water (333 kJ/kg), and r_b is the effective pore radius. The experimental apparent quadruple point temperatures found in this work, the melting points of ice in pores reported by Handa et al.,[13] and T_m^{pore} values given by eq 2 are shown in Figure 6 as functions of reciprocal pore radius. As can be seen in Figure 6, the apparent quadruple point temperatures reported in this work are in good agreement with both the estimates of the ice melting point using eq 2, and the experimental melting points of pore ice obtained by Handa et al.[13]

Frost and Deaton[18] and Holder et al.[19] have calculated enthalpies of dissociation for gas hydrates using the Clausius–Clapeyron or a modified Clausius–Clapeyron equation. These equations are not applicable to processes where different equilibria occur simultaneously, such as the dissociation of gas hydrates in porous media involving broad pore size distributions. Despite this limitation, such calculations may be useful to compare qualitatively the dissociation enthalpy as the nominal pore size changes. As referenced by Handa and Stupin,[8] use of eq 1 along with the Clausius–Clapeyron equation leads to

$$\frac{d[\ln(f/\text{MPa})]}{d(1/T)} = -\Delta H/R = B \qquad (3)$$

Simple rearrangement of eq 3 yields $\Delta H = -BR$, where R is the gas constant; and B is the slope of the linear fits shown in Figure 5, and tabulated in Table 3. The enthalpy of dissociation to liquid water and gas for bulk hydrate and the apparent dissociation enthalpies for pore hydrates in the four silica gel samples considered in this work are plotted in Figure 7. The enthalpies shown in this figure have been corrected to the reference temperature of 273.15 K (as done by Handa and
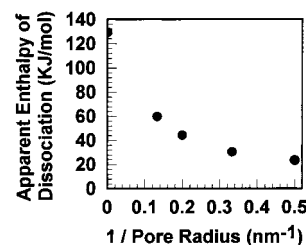

Figure 7. Apparent enthalpies of dissociation for propane hydrate in porous media obtained using the Clausius–Clapeyron equation as a function of reciprocal pore radius. Included is the value for the enthalpy of dissociation in the bulk ($1/r \rightarrow 0$).

Stupin[8] for the calorimetrically measured enthalpies for methane hydrate in pores) using $\Delta H^0 = \Delta H(T) + \Delta C_p(273.15 - T)$, with $\Delta C_p = 0.612$ kJ/mol.[20] Although the data in this figure are purely qualitative, they suggest that the apparent enthalpy of dissociation of the hydrate decreases with decreasing pore size. These changes are similar to the changes in the heat of melting of pore ice that were reported by Handa et al.,[13] who reported decreases in the heat of melting of approximately 16% and 43% in nominal 7.5 and 2.0 nm silica gel pores, respectively.

The hydration numbers (the mole ratio of water to propane in the composition of the hydrate) for SG50, SG30, and SG20 were determined from the pressure–temperature data by the method described by Handa[21] to be 17.99, 17.66, and 17.25, respectively. These are in good agreement with hydration numbers reported for the bulk hydrate,[18,20] which range from 17.0 to 19.7, although no direct comparison can be made because the pressures and temperatures for the conditions under which each of these values is relevant differ from those of the bulk. We note that based on the value of 17.0 reported by Handa[20] for the hydration number under bulk conditions, the hydration numbers observed with SG50, SG30, and SG20 correspond to 94.5%, 96.3%, and 98.6% conversion of pore water to hydrate, respectively, for the samples used to obtain the equilibrium pressure–temperature data reported here.

Summary

This work has shown that equilibrium pressure–temperature data for the dissociation of hydrate in pores of various size distributions can be obtained using a simple experimental setup. The results help to delineate the effect of pore size on the formation and dissociation of propane hydrate in porous media. Handa and Stupin[8] previously studied propane and methane hydrate formation in a silica gel with a nominal pore radius of 7.5 nm. To adequately study the effects of capillary pressure on hydrate formation in small pores requires the consideration of a series of experiments on samples with various nominal pore sizes. In addition, the failure of models presented in the literature[10,11] to accurately predict the observed[8] equilibrium pressures implies that data for a range of pore sizes may be necessary to validate any future models. Uchida et al.,[9] reporting recently on methane hydrate formation in Vycor glass with nominal pore radii of 10, 30, and 50 nm, considered such a series; however, the results for the nominal 30 and 50 nm radius pores were very close to those for the bulk. In this work we have considered a series of pore sizes, all of which clearly show capillary effects. In addition, the measurements of Uchida et al.[9] were for methane (a Structure I hydrate former), but those reported here are for propane (a Structure II hydrate former). In the current study, the equilibrium pressure during dissociation was found to increase as the pore size decreased. Experiments involving two different silica gel samples having the same

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nominal pore size (7.5 nm), but very different particle sizes further substantiates the conclusion that our observations are for hydrate dissociation from the pores, and not from the interparticle spaces. The apparent quadruple point temperatures in the four silica gel samples were found to be consistent with both theoretical and experimental melting temperatures of ice in small pores based on the use of the nominal pore sizes to represent the samples. Calculations based on the Clausius−Clapeyron equation, although only useful for qualitative comparisons, suggest that pore size may have an effect on the enthalpy of dissociation.

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