Interpretation of Ethane Hydrate Equilibrium Data for Porous Media Involving Hydrate-Ice Equilibria

Wu Zhang
U.S. Dept. of Energy, National Energy Technology Laboratory, Morgantown, WV 26507
and
Dept. of Chemical Engineering, West Virginia University, Morgantown, WV 26506

Joseph W. Wilder
U.S. Dept. of Energy, National Energy Technology Laboratory, Morgantown, WV 26507
and
Dept. of Mathematics, West Virginia University, Morgantown, WV 26506

Duane H. Smith
U.S. Dept. of Energy, National Energy Technology Laboratory, Morgantown, WV 26507
and
Dept. of Physics, West Virginia University, Morgantown, WV 26506

Equilibrium pressures for the dissociation of ethane hydrate confined in silica gel pores of nominal radii 7.5, 5.0 or 3.0 nm were measured over a range of temperatures. Each of these porous media contained a broad distribution of pore radii. At higher temperatures, the pressures were larger than previously reported for bulk hydrates, and generally increased with a decrease in nominal pore radius for those data where the equilibria involved liquid water. However, at the lowest temperatures (where the equilibria involved ice), the pressures were identical (within expected experimental uncertainties) for all three silica gels and the same as reported by various authors for the bulk hydrate. The lack of any dependence of the equilibrium pressure on pore size at the lowest temperatures (where the equilibrium involves ethane hydrate, ethane gas, and ice) indicates that, below the quadruple point temperature of the smallest pore in which hydrate formed, there is no detectable effects on the equilibrium pressure due to the restricted geometries of the porous media. It suggests that the interface relevant to the formation of hydrate in silica gel pores is that between the hydrate and aqueous phase (Henry et al., 1999) and that within experimental error the surface energy between the hydrate and aqueous phase can be approximated by that between ice and the appropriate aqueous phase.

Introduction

Clathrate hydrates are solids in which some of the cages formed by the hydrogen-bonded water molecules making up the hydrate lattice are occupied by a small guest-species molecule. Hydrates are formed by methane, ethane, propane, carbon dioxide, hydrogen sulfide, and other components of natural gas. Long studied because they can form in pipelines and block the flow of gas, natural gas hydrates also form in the earth's crust in arctic regions and beneath the seafloor around the margins of most continental shelves. Because of increased drilling in the arctic and in deep ocean waters, natural gas hydrates are now of considerable interest for problems they might cause during the drilling and production for oil or "conventional" natural gas, and also because they represent a potentially huge source of fuel (often estimated to

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Correspondence concerning this article should be addressed to J. W. Wilder.

be larger than all other sources of fossil fuel combined (Sloan, 1997)).

Although hydrates can occur naturally as small nodules of "bulk" material, more often they are dispersed throughout the pores of terrestrial or sub-seafloor sediments (Sloan, 1997). The occurrence of hydrate deposits in porous media has motivated both experimental (Handa and Stupin, 1992; Seshadri et al., 2001; Uchida et al., 1999) and modeling studies (Clarke et al., 1999; Henry et al., 1999) of the effects of pore size on the thermodynamics of hydrate formation and dissociation. Authors of modeling studies have concurred that the thermodynamics of hydrates in porous media should be described by the van der Waals-Plaateuw equation (van der Waals, 1959) for bulk hydrates with the addition of a capillary pressure term of the form $2V_L \cos(\theta)\sigma/r$, where V_L is the molar volume of the aqueous phase, θ is the contact angle between the aqueous phase and the hydrate, σ is the surface tension between the water and hydrate phases, and r is the radius of the pore. To date, both the experimental and theoretical studies have primarily focused on the decomposition of hydrates in porous media to liquid water. Two different ideas for the identity of the capillary interface, and, thus, for the value of the interfacial tension in the capillary pressure term, have been suggested. Moreover, neither value for the tension gave satisfactory agreement (Clarke et al., 1999; Henry et al., 1999) of the modified van der Waals-Plaateuw equation with the experimental data (Handa and Stupin, 1992). This lack of agreement has been attributed to the use of a single value for the pore radius in the predictive equation (Clarke et al., 1999; Henry et al., 1999), even though the porous medium contained a broad range of pore radii (Handa and Stupin, 1992; Handa et al., 1992).

Since the porous media contain various size pores, we propose that each experimental point (P,T) measures the hydrate formation-dissociation equilibrium in a different size pore: what appears to be a line in two-dimensional (2-D) P-T space is actually a line across a P-T-r surface. For most hydrates, the values of all of the parameters in the van der Waals-Plaateuw equation are known; hence, in the modified equation for hydrates in pores, only the values of r (the pore radius), σ (the interfacial tension), and $\cos\theta$ (cosine of the contact angle) are uncertain. Hence, if the value of $\sigma \cos\theta$ can be deduced, the value of r unique to each value of P and T can be calculated from the measured P and T and the van der Waals-Plaateuw equation. Work by our group (Smith et al., 2002) has shown that when the equilibrium is for the dissociation of hydrate to free gas and liquid water, and the correct value of the tension is assumed to be very close to that between liquid and solid water, the pore-size distributions obtained in this way agree very well with pore-size distributions obtained from nitrogen desorption isotherms. (The tension used follows from the hypotheses that the operative surface is between hydrate and liquid water, and that this tension is nearly equal to the tension between ice and liquid water.)

Two groups, Clarke et al. (1999) and Henry et al. (1999), have examined the extension of the standard statistical thermodynamic model used to predict hydrate equilibrium pressures in the bulk to the case of hydrate formation in porous media. The calculations of Clarke et al. (1999) (where the authors assumed a gas/water interface and used a surface tension of 0.072 J/m^2) show definite and significant differences between equilibrium pressures in porous media and those in the bulk when the equilibrium involves ice (see Figures 3 and 4 of Clarke et al. (1999)). Henry et al. (1999) assumed that the relevant interface was between the hydrate and aqueous phases, and used a value of 0.0267 J/m^2 for equilibria involving liquid water. (We note that Klauda and Sandler (2001) present a method for calculation of hydrate equilibrium pressures in a porous media based on a different method, but use the same interface and interfacial tension as Henry et al. (1999a).) The calculations of Henry et al. (1999) were only for temperatures above 273 K, and so did not directly address the decomposition of hydrate to free gas and ice. Clarke et al. (1999) suggest that the equilibrium pressure should be greater in pores than in the bulk even when the equilibrium involves ice. On the basis of the assumption that the surface tension between hydrate and liquid water is nearly that between ice and liquid water, the surface energy effects between hydrate and ice should be very small. As a result, we propose that, at any temperature below its quadruple point, the equilibrium pressure for any size pore should be the same as for the bulk at that temperature. In media with a distribution of pore sizes, the experimental temperature is below the quadruple point temperature of all of the smallest hydrate containing pore, the equilibrium pressure for the sample would be the same as for the bulk. This article presents experimental results for ethane hydrate equilibria in silica gels of three different pore-size distributions that support this hypothesis. As discussed below, the quadruple point temperature decreases with decreasing pore size. The experimental data are used to test the prediction that below the lowest quadruple point for the pores filled with hydrate in the silica gel samples, and the equilibrium pressure-temperature line should be the same for all size pores.

Table 1. Sample Specifications

	Cell No. (Sample Name)		
	1 (3 nm)	2 (5 nm)	3 (7.5 nm)
Volume of the cell,* cm^3	68.7	68.1	68.7
Net wt. of silica gel saturated with water, g	16.54	14.64	10.33
Density of dry silica gel, g/cm^3	0.4898	0.4327	0.4057
Volume of sample, cm^3	33.8	33.8	25.5
Volume of glass beads, cm^3	12.5	19.6	18.0
Head space, cm^3	22.4	14.7	25.2

*Includes the volume of the connecting tubes and valves.

Experimental Methods and Materials

Ethane with minimum purity of 99.95 mol. % was obtained from Matheson. Nitrogen desorption and adsorption studies using Quantachrome Corp Autosorb-1 equipment were used to determine the pore-size distribution (Lowell and Shields, 1991) and pore volume of each of the silica gel samples used in the experiments.

A multiple cell system was constructed to allow for the simultaneous measurement of the equilibrium pressures for three different samples of silica gel. The system consisted of three individual cells, similar to those that have previously been described in the literature (Handa and Stupin, 1992; Seshadri et al., 2001), and which were connected to the same gas inlet via valves. The cells were independent of each other in terms of the cell pressure, but were immersed in the same temperature controlled bath. All three cells were of identical geometry. The working pressure of the multiple cell system was up to 13.6 MPa. The volume of each cell and its connecting tubes and valves ranged from 68.1 to 68.7 cm^3 (Table 1).

The silica gel samples, without any further treatment, were placed in a desiccator containing degassed, distilled water for a period of about seven days to prepare silica gel with sorbed water. The silica gel powder for each cell was mixed with 5-mm-diameter glass beads, and loaded into the cells. The total volume of the glass beads used in each cell has been listed in Table 1. The headspace (the volume of free space internal to the cell, but external to the silica gel sample and glass beads) of each cell was calculated by subtracting the volume of silica gel saturated with water and that of the glass beads from the total volume of the enclosed cell space (Table 1). 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 (1992) for methane and propane hydrates in a silica gel with nominal 7 nm pores, and by Seshadri et al. (2001) for propane hydrate in the three silica gels used in this work.

The cells were placed in a temperature controlled chiller (Fisher Scientific, Model 1028S) with a temperature stability of ±0.01K. The bath temperature was monitored with an Omega *J*-type thermal couple, and was accurate to 0.1°C. All of the experiments reported here had initial temperatures of 243.15 K. At each temperature, equilibrium pressures were measured for all three cells. The temperature was then increased by a small amount and held at that temperature until a new equilibrium was attained in each cell. At each new temperature, pressure readings were taken until the recorded pressure in each cell was constant (to the precision of the transducer used in the experiments (see below)) over a time period on the order of 12 h. The time to reach equilibrium varied for each data point and ranged up to 72 h. During the decomposition of the hydrates, pressure measurements were made with pressure gauges from Duro United: one for pressures less than 100 psig (0.689 MPa), and another for pressures in the range from 90 psig (0.620 MPa) to 600 psig (4.14 MPa). The pressure readings were accurate to within 1% and were measured with a pressure transducer that had been calibrated by the deadweight method.

Table 2. *Pressure-Temperature Data for Equilibria Involving Ethane Hydrate and Ice In Silica Gel Pores of Various Nominal Radii**

3.0 nm		5.0 nm		7.5 nm	
T/K	*P*/MPa	*T*/K	*P*/MPa	*T*/K	*P*/MPa
		243.15	0.112		
				245.15	0.125
246.15	0.137			246.15	0.131
247.15	0.154			247.15	0.143
248.15	0.145			248.15	0.150
249.15	0.158			249.15	0.160
250.15	0.170			250.15	0.170
251.15	0.179	251.15	0.183	251.15	0.179
252.15	0.187	252.15	0.191	252.15	0.186
253.15	0.205	253.15	0.201	253.15	0.196
253.15	0.205			254.15	0.207
254.15	0.222			255.15	0.217
255.15	0.245			256.15	0.227
256.15	0.269			257.15	0.239
257.15	0.290				
258.15	0.316				
259.15	0.345	259.15	0.253		
260.15	0.379	260.15	0.272		
261.15	0.415	261.15	0.284		
262.15	0.452	262.15	0.298	262.15	0.280
263.15	0.493	263.15	0.311	263.15	0.305
264.15	0.534	264.15	0.324	264.15	0.324
265.15	0.582	265.15	0.353	265.15	0.340
266.15	0.634	266.15	0.396	266.15	0.376
267.15	0.677	267.15	0.440	267.15	0.419
268.15	0.755	268.15	0.489	268.15	0.466
269.15	0.821	269.15	0.530	269.15	0.516
271.15	0.968	271.15	0.675	271.15	0.633
272.15	1.049	272.15	0.754	272.15	0.702
273.15	1.142	273.15	0.827	273.15	0.773
274.15	1.236	274.15	0.926	274.15	0.864
275.15	1.330	275.15	1.025	275.15	0.961
276.15	1.423	276.15	1.136	276.15	1.044
277.15	1.504	277.15	1.255	277.15	1.121

*Total measured pressure of gaseous ethane and water.

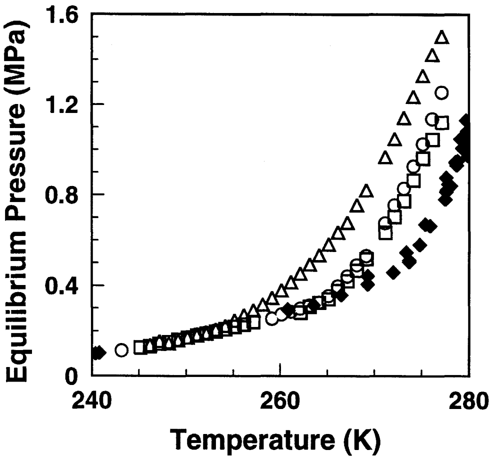

Figure 1. **Experimental equilibrium pressures for ethane hydrate formation in silica gels with nominal pore radii, 3.0 (△), 5.0 (○), 7.5(□) nm, or infinity (◆) (Bulk hydrate, data from Sloan (1997)).**

Results and Discussion

Figure 1 is a plot of the experimental equilibrium pressures for ethane hydrate decomposition in silica gels with nominal pore radii of 3.0, 5.0, or 7.5 nm. Also shown are corresponding data from the literature (which are summarized in Sloan, 1997) for *r* equal to infinity, that is, bulk ethane hydrate. In general, the data qualitatively exhibit the expected increase of equilibrium pressure with increasing values of $1/r$. The data plotted in Figure 1 are tabulated in Table 2. Note the close correspondence of the results for all of the

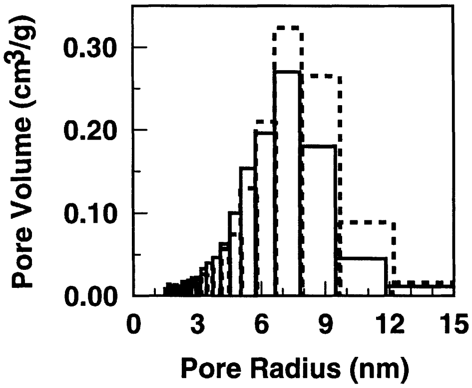

Figure 2. Pore volumes based on nitrogen desorption data for silica gels with nominal 7.5 nm (.....) or 5.0 nm (—) pore radii.

silica gel samples and the bulk data at low temperatures (when the equilibria would be expected to involve ice). This range of correspondence varies from sample to sample due to the different pore-size distributions present in the various samples and the effect of pore size on the freezing point of water (see discussion below).

We also note the close correspondence of the data for the silica gels with pores of nominal 7.5 nm and 5.0 nm radii up to a temperature of 269.15 K. Such correspondence could be surprising in light of the expected increase in equilibrium pressure with a decrease in pore radius. Figure 2 shows the pore-volume distributions of these two media calculated (by the method described in Lowell and Shields (1991) from our nitrogen adsorption data. As can be seen, the two distributions are identical up to a pore radius of about 6 nm. Equilibria involving pores up to this size would lead to the close correspondence of the observed equilibrium pressures. From this, we infer that, below 269.15 K, the equilibria are for radii smaller than 6 nm.

We have four goals for interpretation of the data in Table 2: (1) to discern which data are for the equilibrium of hydrate with liquid water and free ethane gas, and which data are for the equilibrium of hydrate with ice and free gas; (2) to compare the data for the hydrate/ice-plus-gas equilibrium in various sized pores with corresponding data for the bulk hydrate and show that there is no discernable difference; (3) to suggest a possible interpretation of why the low-temperature pore data give the same equilibrium pressure as bulk data; and (4) to explain why previous (Handa and Stupin, 1992) data in the literature seemed to show a difference between bulk and pore hydrates for the dissociation to ice.

Discriminating between equilibria involving hydrate-ice or hydrate-water

While a bulk hydrate has a unique quadruple point, hydrate in a porous medium with a broad distribution of pore sizes does not. The latter point is clarified for our samples by Figure 3. As determined (Lowell and Shields, 1991) from our measured nitrogen desorption isotherms, Figure 3 illustrates the pore volume as a function of pore radius for our silica gels of nominal pore radii 7.5 nm, 5.0 nm, and 3.0 nm. Note that in Figure 3 the height of each vertical bar represents the pore volume for the pores having radii in the range indicated by the width of the bar. For gases with negligible water solubilities, the quadruple point temperature is closely given by the melting point of water. Since the effect of a restricted geometry on the melting point of a pure substance is well known (Clennell et al., 1999), the quadruple point temperature T_{Q1} can be expressed as a function of the pore radius r

$$T_{Q1}(1/r) = T_{Q1}(0)(1-2\sigma/\rho\Delta Hr) \tag{1}$$

where $T_{Q1}(0)$ is the quadruple point of bulk water (which, for hydrates formed from a gas with negligible water solubility, is 273.15 K), ρ is the density of water (1,000 kg/ m^3), σ is the

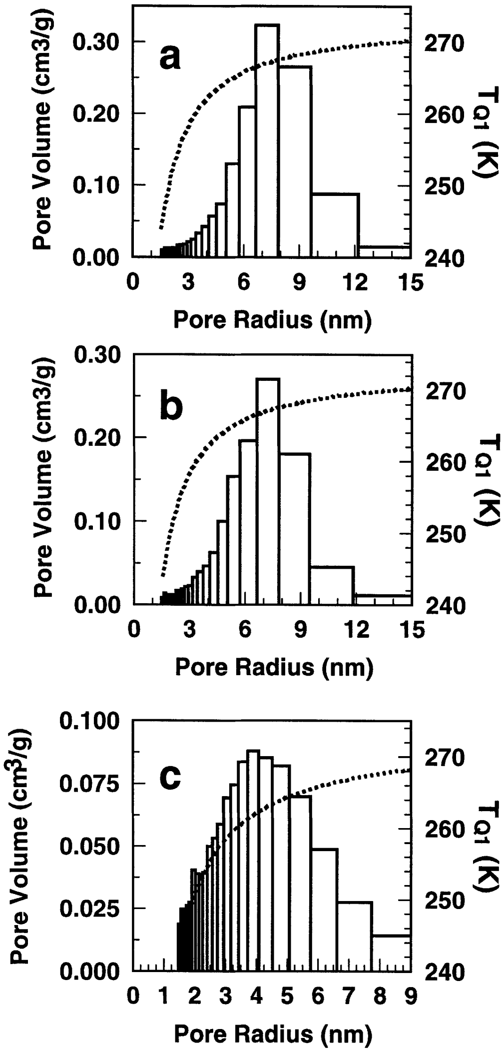

Figure 3. Pore volume as a function of pore radius (as measured by nitrogen desorption isotherms) for silica gels of nominal pore radii (a) 7.5 nm, (b) 5.0 nm, (c) 3.0 nm.

Also shown (dotted traces) are plots of the quadruple point temperature T_{Q1} as a function of the pore radius r, illustrating which pores of each silica gel are above or below their $T_{Q1}(r)$ for any temperature T.

surface tension (0.0267 J/m^2) between water and ice (Clennell et al., 1999), and ΔH is the specific enthalpy of fusion of bulk water (333 kJ/kg). In Eq. 1 it is assumed that the capillary surface is a spherical cap. Other geometries would require a constant different from "2" in the numerator of the second term on the righthand side. Plots of the quadruple point temperature for various pore radii calculated from Eq. 1 have been superposed on the distributions shown in Figure 3. Together, the various plots of Figure 3 illustrate for any temperature T which pores of each hydrate-silica gel sample are above or below their $T_{Q1}(1/r)$. For example, for a temperature of 262 K, it can be seen from Figure 3a that only a small fraction of the pores (those with radii below approximately 4 nm) in the nominal 7.5 nm sample would contain liquid water, while a significant fraction of pores present in the nominal 3 nm sample would contain liquid water.

As shown elsewhere (Wilder et al., 2001a), the usual treatment of the van der Waals-Plaateuw equation predicts that, except for very small higher-order terms, for bulk hydrates (with a single guest component), the logarithm of the equilibrium guest fugacity on either side of the quadruple point temperature should be a linear function of $1/T$

$$\ln\,(f_i/\text{MPa}) = a_i + b_i/T \tag{2}$$

Empirical relations of this or similar forms have previously been reported in the literature (Kamath, 1984; Parrish and Prausnitz, 1972; Sloan, 1997), but prior to recent work (Wilder et al., 2001a) had not been shown to be derivable from a standard statistical thermodynamic model. Figure 4a contains a plot of $\ln(f_i/\text{MPa})$ vs. 1/T for the bulk ethane hydrate data of Figure 1 and a regression of Eq. 2 to the data. All of the fugacities presented in this work were calculated using the Soave-Redlich-Kwong equation of state (Soave, 1972). The values of a, b, and the regression coefficient R for the regression in Figure 4a for the bulk data are listed in Table 3. It is apparent that Eq. 2 provides an excellent fit to the bulk data, and we anticipate that the published data for bulk ethane hydrate will be an accurate basis for comparison of corresponding data for ethane hydrate in pores. Figure 4b shows a similar plot for the experimental data reported in Table 2 and in Figure 1. Also shown are the bulk data lying in the indicated domain. Note that the data for each nominal pore size separate into two distinct segments. The segments which lie on top of the bulk ice-hydrate line presumably involve equilibria involving ice and hydrate in the respective silica gel pores. The data which lie above the bulk data would then correspond to equilibria involving water and hydrate. Based on the evidence in Figure 4b, we have separated the data by classifying them as belonging to one of the two types of segments discussed above. In this manner we propose that, in the experiments reported here for the nominal 7.5 nm silica gel, the data in Table 2 corresponding to temperatures less than or equal to 266.15 K were for equilibria involving hydrate and ice, while, for the 5.0 and 3.0 nm silica gels, only points corresponding to temperatures less than or equal to 265.15 K and 252.15 K, respectively, involved ice. All of the other data in Table 2 correspond to equilibria involving hydrate and liquid water.

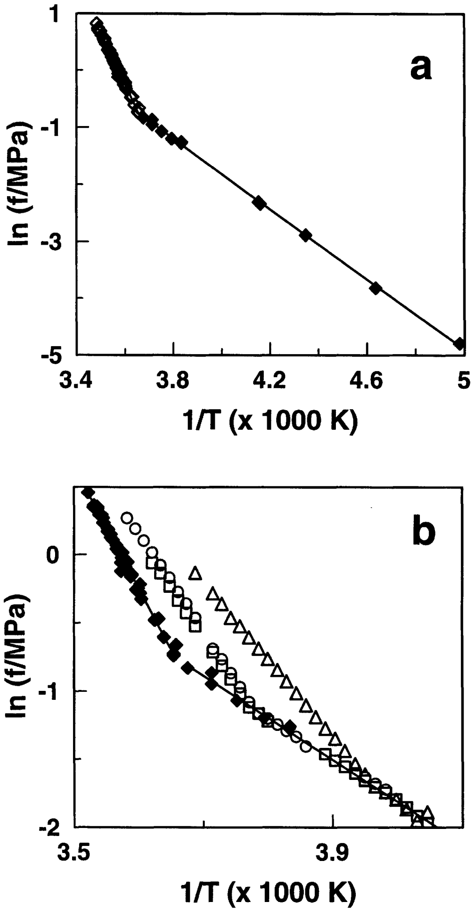

Figure 4. Plots of ln (f/MPa) vs. 1/T of data in Figure 1 for (a) bulk ethane hydrate data and (b) pore hydrate data in silica gels with nominal pore radii of 3.0 (△), 5.0 (○), or 7.5(□) nm.

Comparison of bulk and pore data for hydrate-ice equilibria

Figure 5 is a plot of ln (f_i/MPa) vs. $1/T$ for ethane hydrate in silica gels of various nominal pore sizes, along with the corresponding data for bulk ethane hydrate. The temperature range of Figure 5 is restricted to the condition that $T < T_{Q1}(1/r)$, so that only data for the dissociation to free gas and

Table 3. Values of a_i and b_i in the Equation ln $(f_i/\text{MPa}) = a_i + b_i/T$ for Ethane Hydrate in Silica Gel Pores of Various Nominal Radii, r_i

r_i	a_i	b_i(K)	*R_i	No. of Data
3.0 nm	10.26	−3,018	0.9525	7
5.0 nm	10.59	−3,101	0.9971	11
7.5 nm	10.64	−3,116	0.9971	19
infinity†	10.52	−3,084	0.9996	12
Avg., this work	10.57	−3,096	0.9966	37
Avg., all data	10.52	−3,085	0.9992	49

*Regression coefficient.
†Bulk hydrate.

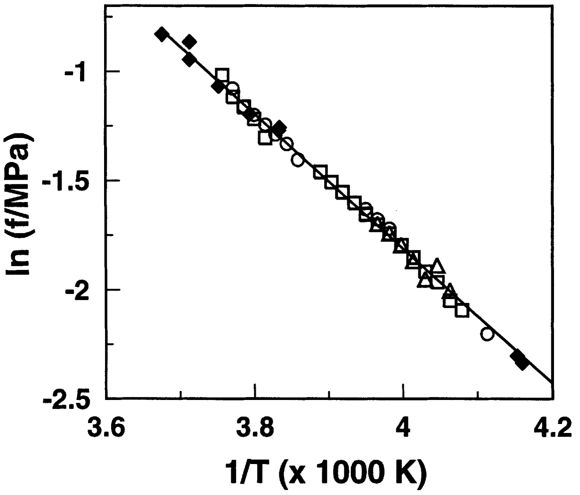

Figure 5. Plots of ln (f_i/MPa) vs. 1/T for bulk (◆) ethane hydrate (taken from Sloan (1997)) and for ethane hydrate in silica gels of nominal pore radii 3.0 (△), 5.0 (○), or 7.5(□) nm, for temperatures below $T_{Q1}(r)$ of the smallest-radius pores in which hydrate formed.

Note that the regressions of the equation $\ln(f_i/\text{MPa}) = a_i + b_i/T$ to the bulk (solid trace) and pore (dotted trace) data are indistinguishable.

ice are included. Also shown are regressions of the equation $\ln(f_i/\text{MPa}) = a_i + b_i/T$ to each set of data for the various silica gels. The values of a_i and b_i for the hydrate in the porous media are listed in Table 3. It is readily apparent from Figure 5 and Table 3 that for sufficiently low temperatures and the particular experimental procedure utilized here, there is little difference between the equilibrium pressures for the bulk hydrate and the pressures for the ethane hydrate in the various porous media. In determining the fits in Table 3, data for the nominal 7.5 nm silica gel for temperatures less than or equal to 266.15 K from Table 2 were used, while, for the 5.0 and 3.0 nm silica gels, only points corresponding to temperatures less than or equal to 265.15 K and 252.15 K, respectively, were used. In addition, a fit of Eq. 2 to all of the data for ethane hydrate in pores (dotted trace) is shown in the figure, although it is indistinguishable from the regression lines for the bulk data, or for the individual sets of pore data. The results shown in Table 3 clearly indicate that, for sufficiently low temperature ranges, there were no detectable differences between the observed equilibrium pressures for ethane hydrates in various size silica gel pores and the equilibrium pressures for the bulk hydrate at the same temperatures. The specifics of the various regressions performed to construct Table 3 are as follows.

As listed in Table 3, for 12 points for the bulk hydrate, the value of a_i was 10.52; for the porous media, the values of a_i were 10.64 (19 points), 10.59 (11 points), and 10.26 (7 points), respectively, for the nominal 7.5, 5.0, and 3.0 nm porous media. For all 37 points for the porous media, the value of $a_i = 10.57$, compared to $a_i = 10.52$ for the 12 bulk hydrate data. For the various porous media, the values of b_i ranged from $-3{,}018$ to $-3{,}116$, with $b_i = -3{,}096$ for all of the porous-media data considered as a single group; these values may be compared to $-3{,}084$ for the bulk hydrate. There may be a systematic variation in a_i and b_i with average pore size, but any such variation, if present, is very small and may be due to a systematic error in reading the equilibrium pressure at lower temperatures where the smallness of the pressure could lead to larger relative errors. The consistency in the values of a_i and b_i for these various regressions strongly suggests that the results for the pore hydrates are indistinguishable from the bulk results over the temperature ranges indicated above.

Interpretation of low-temperature data

Figure 5 of this work strongly suggests that, when the equilibrium involves ice, there is no detectable difference between the equilibrium pressures for ethane hydrate formation in silica gel pores and those in the bulk. As is clear in Figures 1 and 4b, at higher temperatures (where the equilibrium would involve liquid water), there is a significant increase in the equilibrium pressure for hydrates in the silica gel pores. There are several possible explanations for the correspondence of the low-temperature pore data with the bulk data. One possible explanation suggested by an anonymous reviewer is that the system was not yet at equilibrium, and, therefore, the measured pressures were not the true equilibrium pressures. Due to the length of time that was allowed to pass in order to ensure that the recorded pressures were stable (see the experimental section above), we believe that the system was at thermodynamic equilibrium.

Another suggested explanation for the correspondence of the pore and bulk data at low temperatures is that, by some mechanism, the equilibria at low temperatures involved a flat interface removing any capillary effects. For example, the hydrate in the sample might not have been in the pores, or, as suggested by Uchida et al. (2002), one could hypothesize the presence of a hydrate cap covering the pore openings. This would result in the equilibria involving essentially bulk hydrate residing on the outside of the silica gel (covering the pores). While there is no way that we can definitively state that all of the equilibrium pressures reported in this work resulted from equilibria involving pore hydrate, the increases of the equilibrium pressures at higher temperatures above those for bulk hydrate do indicate the presence of pore hydrate in the sample. In addition, the amount of water taken up by the silica gel prior to hydrate formation was within 1% of the total pore volume reported for the silica gels by the manufacturer. This, combined with the experimental method used to prepare the hydrate sample, as well as the evidence from previous experiments (using the same method) where the hydrate was clearly in the pores (Smith et al., 2002; Wilder et al., 2001b), all seem to suggest that hydrate was formed in the pores. While we cannot rule out the possibility that there might have been a small amount of hydrate formed over the mouth of some of the pores in the media, it is difficult to imagine a scenario where the large quantity of hydrate necessary to account for the amount of gas liberated in the experiments reported in Figure 4b where the equilibria are proposed to involve ice could have all resided in caps over the mouths of the silica gel pores. If one supposes that the equilibrium pressure for hydrate-ice equilibria is dependent on the pore size, then capillary effects would result in pore hydrate dissociating prior to any bulk-like hydrate, thereby leading to equilibrium pressures above those reported for the bulk. Thus, such a cap as proposed by Uchida et al. (2002) would have to reside over all of the pores simultaneously in order to keep any of the pore hydrate from dissociating. Not only would all of the pores have to be covered by such a cap, but the cap would also have to be thick enough and strong enough to be able to maintain the required pressure difference between the inside of the pore (where this hypothesis assumes the equilibrium would require a higher equilibrium pressure relative to the bulk) and the external gas pressure. While more studies need to be done to incontrovertibly resolve this issue, there is currently no experimental evidence which supports such a complex hypothesis. Both the data reported in this work, and those for methane hydrate in 30 nm (diameter) porous glass reported in Uchida et al. (1992), can be interpreted using our simpler explanation. To better resolve this issue, more conclusive experimental evidence needs to be presented which either confirms or refutes our simple explanation.

The implications of our model for hydrate equilibria in porous media are (Smith et al., 2002; Wilder et al., 2001b): (1) the product σ $\cos(\theta)$ (the surface tension times the cosine of the contact angle) for equilibria involving liquid water and hydrate can be approximated by that between water and ice (0.0267 J/m^2); (2) that for equilibria between ice and hydrate, this product is sufficiently small to be approximated as zero.

The first of these implications has been tested by constructing pore volume distributions from hydrate data and comparing them to those obtained from nitrogen desorption studies (Smith et al., 2002; Wilder et al., 2001b). Such comparisons have shown very good agreement, suggesting that the value of $\sigma\cos(\theta)$ can be approximated as 0.0267 J/m^2. The results presented in this work, as well as those for methane hydrate in 30 nm (diameter) porous glass reported in Uchida et al. (1992), seem to support the second hypothesis, namely that $\sigma\cos(\theta)$ is not significantly different from zero when the equilibrium involves ice. This leads to equilibrium pressures that agree with those observed in the bulk, regardless of the size of the pore in which the hydrate resides. We note that Uchida et al. (1992) state that, "Although the experimental results obtained in the present study look as if they support their (Wilder et al., 2001b) prediction, we consider the interfacial tension between ice and hydrate to not be zero as discussed above. Further experimental efforts and discussions are required to clarify the nature of the equilibrium conditions of gas hydrates in small pores below the quadruple point" (parenthetical comment added for clarity). Uchida et al. (2002) have proposed the value of 0.041 J/m^2 for the surface energy between hydrate and ice, based on previous results involving the examination of air hydrate crystals trapped along ice grain boundaries (Uchida et al., 1993). Accepting this value for the surface energy between ice and hydrate, we are left to conclude that in both our experiments reported here, and in those of Uchida et al. (2002), the cosine of the contact angle between the hydrate and ice at the pore wall must be sufficiently small as to make $\sigma\cos(\theta)$ negligible.

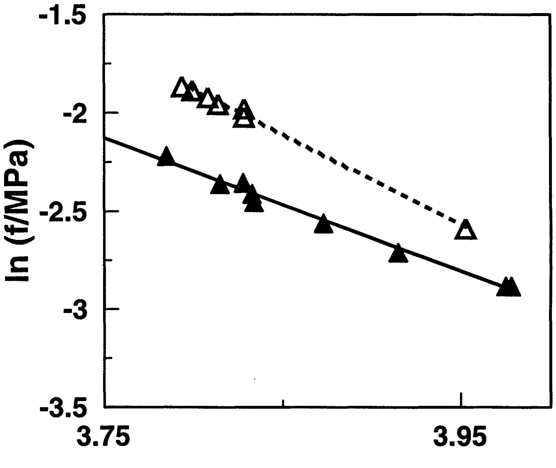

Figure 6. Plots of ln (*f*/MPa) vs. 1/*T* for the propane hydrate data of Handa and Stupin (1992) in nominal 7 nm silica gel pores (△), as well as for bulk propane hydrates (▲).

Also shown are the best linear fits to these data.

Reconciliation of present and past data

Comparisons of data for bulk hydrate and for hydrate in pores must be for the same equilibrium. As discussed elsewhere (Smith et al., 2002; Wilder et al., 2001b), when the equilibrium involves liquid water, the equilibrium pressure measured for a porous medium can involve a different radius pore at each temperature, and, therefore, may represent a fundamentally different equilibrium. However, the results given in this work suggest that the pressures for equilibria involving hydrate and ice are independent of pore size. Earlier experimental results (Handa and Stupin, 1992) for methane and propane hydrates in 7 nm nominal radius silica gels showed equilibrium pressures above those for the bulk for all of the temperatures at which pressures were measured. Handa and Stupin suggested that some of their data were for equilibria involving ice. This seeming discrepancy between previous results and those presented in this work and elsewhere (Uchida et al., 2002) needs to be addressed.

Figure 6 shows a plot of ln (f/MPa) as a function of $1/T$ for the data of Handa and Stupin (1992) for propane hydrate in silica gel with nominal 7 nm radii pores. They proposed that some of these data represented equilibria involving ice. Also shown are the bulk data for equilibria involving ice, hydrate, and free gas. Note that there is a significant difference between these two sets of data, although the pore data do seem to approach the bulk data as T decreases (which corresponds to an increase in $1/T$). While the interpretation of Handa and Stupin's data (Figure 6) could lead one to conclude that pore size has an effect on the equilibrium pressure even when the equilibrium involves ice, our data (Figure 5) indicate that, for equilibria involving ice, there is no measurable difference between the equilibrium pressure in nominal 7.5 nm silica gel pores and that in the bulk. We believe that the resolution of this seeming inconsistency involves the initial temperature at which the experiments were started, and the pore-size distribution present in the media. Since the series of equilibrium measurements is started at low temperature and proceeds by raising the bath temperature, the data at the lowest temperatures represent the first hydrate to dissociate, which would be that hydrate in the smallest pores. It seems plausible that the low temperature data points of Handa and Stupin (1992) (where one might have expected to find ice in equilibrium with the hydrate) involved the smallest pores, which necessarily have the lowest ice melting points (see Eq. 1). If the melting point in the size pore involved in a specific equilibrium measurement was lower than the experimental temperature, the equilibria would have involved liquid water, not ice, and the capillary effect described above would then cause the increase in the equilibrium pressure (relative to the bulk) reported by Handa and Stupin (1992). By starting our experiments at a temperature that was 10 K below that used by Handa and Stupin (1992), the experimental temperature for some of our data was below the quadruple point for the size pore involved in the equilibria. For example, Eq. 1 predicts that only pores with radii less than 1.4 nm would contain liquid water at an initial temperature of 243 K (the initial temperature in our experiments), while pores with radii up to nearly 2.2 nm would contain liquid water at 253 K (the lowest temperature for Handa and Stupin's experiments). As can be seen in Figure 3a, there is a small but finite amount of pore volume in the range below 2.2 nm that could have been involved in the initial point of Handa and Stupin at 253 K, while there is no measurable volume in pores with radii less than 1.4 nm. We believe that the interaction of the pore-size distribution with the initial experimental temperature allowed us to obtain data for hydrate formation in porous media that was in agreement with bulk ethane hydrate data (see Figure 5).

Summary

We have previously predicted that the dissociation of hydrate to ice and free gas in porous media should be independent of pore size, and that the associated equilibrium pressures should agree with those observed for the bulk. This prediction was recently supported by the data of Uchida et al. (2002) for methane hydrate in porous glass with nominal pore radii of 15 nm. We have here presented equilibrium pressure data for ethane hydrates in silica gel pores with nominal radii of 3.0, 5.0, or 7.5 nm. While data in the liquid-water region showed the expected dependence on pore radius, the data for equilibria involving ice showed no dependence on pore radius, and they are in excellent agreement with previous results for bulk hydrates (summarized in Sloan (1997)). This result suggests that there is no detectable surface stress affect between the hydrate and ice, suggesting that $\sigma \cos(\theta)$ is sufficiently small so as to be negligible. We believe that this result further supports the use of 0.0267 J/m^2 to approximate the interfacial tension between hydrate and liquid water. In summary, we conclude that for the equilibrium of ethane hydrate with ice and free gas the equilibrium pressure was independent of pore size, and was indistinguishable from the equilibrium pressure for bulk hydrate at the corresponding temperature.

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