Equilibrium Pressures and Temperatures for Equilibria Involving sI and sII Hydrate, Liquid Water, and Free Gas in Porous Media

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Equilibrium pressures were measured over a range of temperatures for dissociation to free gas and liquid water of various sI (methane, ethane, and carbon dioxide) hydrates and one sII hydrate (propane) confined in silica gel pores of nominal radii 7.5, 5.0, or 3.0 nm. Each of these porous media contained a broad distribution of pore radii. At higher temperatures, two effects were observed: (1) the pressures for the hydrate in porous media were larger than the pressures previously reported for the bulk hydrate; and (2) in general, the pressure difference between a hydrate in the bulk and in a porous medium increased with a decrease in the nominal pore radius of the medium. We have shown how the van der Waals-Platteeuw equation for bulk hydrates, when modified to include the capillary pressure effect of the pores, can be used to calculate the distribution of pore sizes in the various porous media. These pore-size distributions agreed with values measured by conventional nitrogen desorption isotherms. These agreements have several implications: (1) the modified equation is valid for the data; (2) the correct value of the interfacial tension was used in the calculations; (3) the operative interface in the capillary pressure was between hydrate and water; and (4) that in most cases the hydrate was equally distributed between the pores that contained hydrate in each silica gel sample. These conclusions were found both for the sI and sII hydrates that were studied. In this interpretation, each experimental point, for which a value of temperature (T), and pressure (P) is directly measured, also is associated with the equilibrium for a different pore radius r. Simple plots of P vs. T represent the directly measured parameters, but they are very misleading because the experimental path was actually across a $P(T,r)$ surface and along this path r was not constant. Thus, our method appears to correctly treat the experimental data to give the true $P(T,r)$ path taken on the $P(T,r)$ surface for hydrates in porous media. These studies also clarify that when data for hydrates in porous media are represented in misleading P vs. T plots, (1) experimental results may appear to be in conflict when actually they are not, and (2) data may appear to agree, when in fact they do not.

1 Introduction

Gas hydrates can be formed from light hydrocarbons and water at high pressures and ordinary temperatures (or at moderate pressures and low temperatures). The discovery of natural gas hydrate deposits in arctic regions and in sub-seafloor deposits in outer continental shelves has stimulated interest in the study of gas hydrate formation/decomposition in porous media. 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.

The study of the synthesis and decomposition of gas hydrates in porous media is important to gaining an understanding of the conditions at which gas hydrates form or dissociate in gas reservoirs. Several such studies have been reported in the literature. Studies by Makogon (1981) in sandstones with nominal 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. Since the equilibrium pressure for the dissociation of hydrates and the thermodynamic properties in large pores are apparently nearly identical to those in the bulk (Kamath, 1984), one needs to conduct experiments in much smaller pores to quantify pore-size effects. Interfacial forces and ifferences in chemical potentials 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 dissociation characteristics of the hydrate. Therefore, the study of hydrate formation /dissociation is much more complex for porous media than for the bulk. Handa and Stupin (1992) studied methane and propane hydrates in silica gel of 7.5 nm nominal pore radius, and Uchida et al. (1999) investigated the properties of methane hydrate in three porous Vycor glass samples with pore radii of 25 nm, 15 nm, and 5 nm. Recent work has presented measurements for methane (Smith et al, 2001a) and propane (Seshadri et al., 2001) hydrate formation in silica gels of nominal pore radii of 7.5 nm, 5.0 nm, or 3.0 nm..

Henry et al (1999) and Clarke et al (1999) have proposed interpretations of the data of Handa and Stupin (1992) based on the addition of a capillary pressure term to the statistical-thermodynamic model of van der Waals and Platteeuw (1959). However, these interpretations did not adequately reproduce the experimental equilibrium pressures of Handa and Stupin (1992) due to the assumption of a single pore size to represent the porous medium. Because hydrates formed in porous media have one additional degree of freedom, the equilibrium curve in *P-T* space of bulk hydrates is replaced by an equilibrium surface in *P-T-r* space, the quadruple point is replaced by a quadruple line, and simple regressions to experimental *P-T* data can not be used to find the resulting multiple quadruple points.

To solve the problems of assuming a single pore size, we propose a modified model that recognizes the broad distribution of pore sizes present in many porous media. This model, in addition to explaining the source of previous discrepancies, also allows the reconstruction of the pore volume distribution present in the porous medium. We have performed experiments and investigated the properties of several hydrates in the same silica gel samples (nominal pore radii of 3, 5, and 7.5 nm). These data allow a test of the multiple pore-size model for both Structure I and Structure II hydrates. Such data for a range of pore sizes, all of which involve capillary effects that strongly affect the equilibrium pressure, should help to further delineate the effects of pore size on key equilibria for important components of natural gas.

2 Experimental Methods

A high pressure cell (Seshadri et al., 2001) about 30 ml in volume was loaded with around 140 5-mm-diameter glass beads, and a slurry consisting of liquid nitrogen and silica gel saturated with 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 minutes to remove air. The cell was transferred to a temperature controlled chiller (Neslab Model RTE 140), and then connected to the gas 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 experimental methods used to form the hydrate and to measure the equilibrium temperatures and pressures during its subsequent dissociation are the same as those used previously (Handa and Stupin, 1992; Seshadri et al., 2001), and entail a stepwise increase of the temperature and the subsequent reestablishment of equilibrium at each new temperature.

3 Results and Discussion

The equilibrium pressure-temperature data for the silica gel samples (corrected for the vapor pressure of water) are shown graphically in Figure 1 for propane (Seshadri et al, 2001), Figure 2 for methane (Smith et al, 2001a), and Fig. 3 for carbon dioxide (Smith et al, 2001b). (For data on ethane hydrate, see Zhang 2002.) Also included in the Figures are measured data for bulk hydrate (Sloan, 1997). In Figure 2, some of the data for the silica gels having nominal pore radii of 5.0 or 7.5 nm appear to coincide. The equilibrium pressure at a specific temperature is expected to depend on the pore radius for such sized pores as those considered here (Makogon, 1981; Seshadri et al., 2001). Furthermore, if the data for the nominal 7.5 nm pores presented in Figure 2 are compared with the data in the literature (Handa and Stupin, 1992), there is a small difference that increases as the temperature increases. Both of these apparent discrepancies can be explained by means of a conceptual

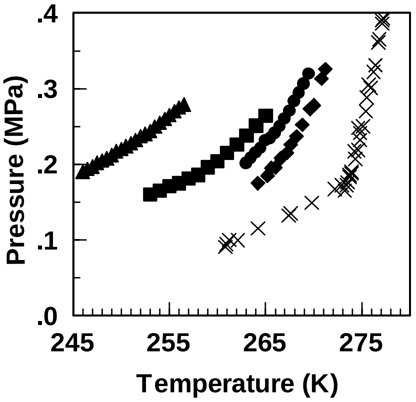

Fig. 1: Experimentally measured equilibrium pressures in silica gels of nominal pore radii 2 (▲), 3 (■), 5 (●), or 7.5 (◆) nm for propane hydrate. Also shown are results for bulk hydrate formation (×).

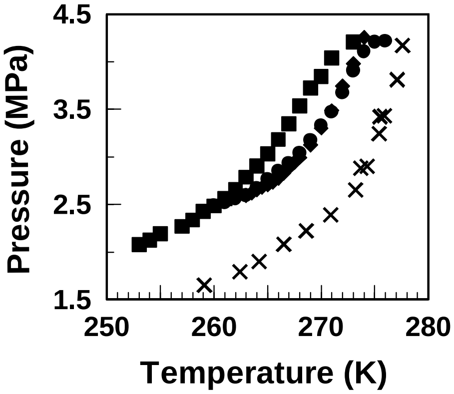

Fig. 2: Experimentally measured equilibrium pressures in silica gels of nominal pore radii 3 (■), 5 (●), or 7.5 (◆) nm for methane hydrate. Also shown are results for bulk hydrate formation (×) .

model for hydrate decomposition in a porous medium involving a broad pore-size distribution (Smith et al, 2001a).

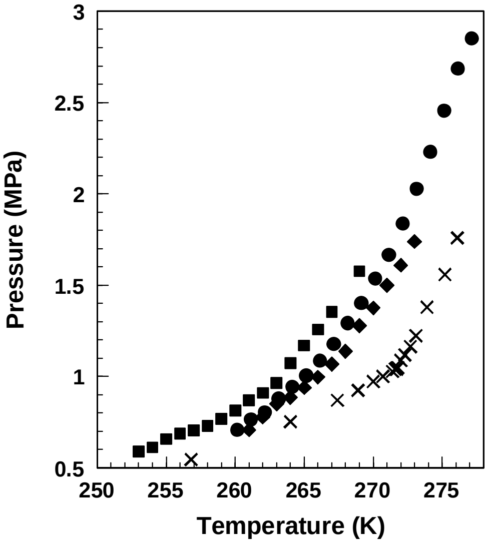

Fig. 3: Experimentally measured equilibrium pressures in silica gels of nominal pore radii 3 (■), 5 (●), or 7.5 (◆) nm for carbon dioxide hydrate. Also shown are results for bulk hydrate formation (×) .

If the modifications suggested by Henry et al. (1999) to model hydrate formation in porous media are made to the standard statistical thermodynamic model used for bulk hydrates the result can be written in the form of eq. (1) (See Wilder et al, 2001 for details):

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{RT_f} dP - \ln(\gamma_w X_w) + \sum_{\mathrm{i}} \eta_{\mathrm{i}} \ln(1 - Y_i) + V_L \frac{2\cos(\theta)\sigma_{hw}}{rRT_f} = 0 \qquad (1)$$

A very different approach involving a completely different method of predicting hydrate equilibria and which imposes an assumed pore size distribution has been proposed by Klauda and Sandler (2001). In this paper we demonstrate the use of eq. (1) along with equilibrium temperature-pressure data to determine what size pores are involved in the equilibria observed experimentally for hydrates in porous media such as silica gel. In eq. (1), T_f and P_f are the temperature and pressure at which the hydrate forms, T_0 is the temperature of the standard reference state (T = 273.15 K, P = 0), and $\Delta\mu_W^0$ is the chemical potential difference for the reference state. The second term on the left hand side of eq. (1) accounts for the temperature dependence of the chemical potential difference (at zero pressure) by assuming $\Delta H_W = \Delta H_W^0 + \int_{T_0}^{T} \Delta C_p(T')dT'$, where ΔH_W^0 is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature. The temperature dependence of the heat capacity difference between these two states is modeled as (Holder et al., 1988) $\Delta C_p(T') = \Delta C_p^0 + b(T' - T_0)$, where ΔC_p^0 is the reference heat capacity difference, and b is a constant. The third term on the left-hand side of eq. (1) corrects for the pressure dependence, and involves ΔV_W, the volume difference between the empty hydrate and pure solid or liquid water (at T_0), and is assumed constant (but different for solid or liquid water). The fourth term is a correction to the chemical potential of pure water due to the solubility of the guest molecule (which can be neglected for methane and propane (Munck et al., 1988)). We note that the maximum errors between the experimental data and the model predictions for bulk hydrate formation are 1.3 and 2.6 percent for methane and propane, respectively, over a temperature range from 260 to 276 K using the model parameters given in Table 2 of Smith et al (2001a) and ignoring the gas solubility in water. The fifth term involves η_{i}, which is the number of cavities of type i in the hydrate lattice. Y_i denotes the probability of a cavity of type i being occupied by the guest molecule, and is given in terms of the fugacity of the hydrate guest in the gaseous state (f) and the Langmuir adsorption constant (C_i) by $Y_i = \frac{C_i f}{1 + C_i f}$. In the present model the temperature dependence of the Langmuir constants is accounted for by using the form presented by Munck et al (1988), $C_i = \frac{A_i}{T}\exp(B_i/T)$, where A_i and B_i are experimentally fit parameters, and are dependent on which guest molecule is present. Other researchers have used Kihara potential functions to model these constants. Since this approach also involves parameters that are adjusted to fit the model predictions to experimental data, we use the above formulation due to its ease of use. The last term on the left-hand side of eq. (1) shows the effect of capillary pressure on the chemical potential difference between the empty hydrate lattice and the pure water phase. Here, V_L is the molar volume of water in the pure water state, θ is the wetting angle between the pure water phase and the hydrate (Henry et al, 1999), σ_{hw} is the surface tension between the water and hydrate phases (Henry et al, 1999), and r is the radius of the pore. Eq. (1), along with the data in Fig. 1, 2 or 3 can be used to calculate the effective pore radius involved in each equilibrium. These calculations are based on the following conceptual model for hydrate decomposition in a porous medium with a broad pore-size distribution. As a simplistic representation of such a medium, consider a bundle of tubes with a distribution of tube radii $r_1 < r_2 < r_3 < r_4 < r_5 \ldots$. If we had a series of samples each made up of exclusively one size tube, then the equilibrium pressures necessary to stabilize the hydrate in the various samples would be given by $P_1, P_2, P_3, P_4, P_5 \ldots$, with $P_1 > P_2 > P_3 > P_4 > P_5 \ldots$. A more realistic representation of porous media includes a distribution of these tubes of different radii such that in a given sample there are N_i tubes of radius r_i. Let the total volume of gas present (as hydrate) in tubes of radius r_i be equal to V_i^g. Now consider a sample of a porous medium with various size tubes where the tubes are filled with hydrate and the reaction chamber is kept under conditions such that the hydrate is stable for all tube sizes. As the temperature is raised, the point will eventually be reached where the gas pressure in the chamber is not sufficient for all of the hydrate to remain stable, and some of it will start to decompose. Since smaller radii tubes require larger pressures for their hydrate to remain stable, hydrate in the smallest tubes will be the first to decompose. As the hydrate in the smallest tubes decomposes, gas is given off, raising the pressure in the headspace (the free space exterior to the porous medium and interior to the reaction chamber). If the volume V_1^g (the total volume of gas available from tubes of radius r_1) is more than sufficient to raise the pressure up to P_1 (the pressure necessary to stabilize the hydrate in tubes of radius r_1 at the current temperature), then equilibrium will be re-established before all of the tubes of radius r_1 are exhausted, and the experimentally observed pressure at this temperature will be that which would be observed if the medium were solely made up of tubes having this radius. If, due to the volume of the headspace, these tubes do not contain a large enough volume of gas to raise the pressure by the required amount, then all of the hydrate in tubes of this size will decompose, and that in the next size tubes (having radii r_2) will begin to decompose. If the total volume from these two tube sizes ($V_1^g + V_2^g$) is more than sufficient to raise the pressure up to P_2, then not all of the hydrate in this size tube will decompose, and the experimentally observed pressure at this temperature will be that which would be observed if the medium were solely made up of tubes having radius r_2. Therefore, with this conceptual model for hydrate decomposition in porous media, at each temperature the measured equilibrium pressure corresponds to that for a single size tube, but the size of the tube will vary as the temperature is varied. In addition, exactly which size tube is involved in the equilibrium at a specific temperature will depend on the relative sizes of the headspace and the amount of gas present in the form of hydrate.

For each point (T_i,P_i) of the pressure equilibrium curves in Figs 1-3 there is a corresponding r_i that can be found from eq. (1) that allows the model to exactly reproduce the measured equilibrium pressure. Fig. 4 shows the results of these calculations for propane hydrate. Shown in Fig. 4 are the (T_i,P_i,r_i) points generated using the experimental (T_i,P_i) data to determine the corresponding radius for each experimental point. Also shown is a portion of the $P,T,r)$ surface generated using eq. (1).

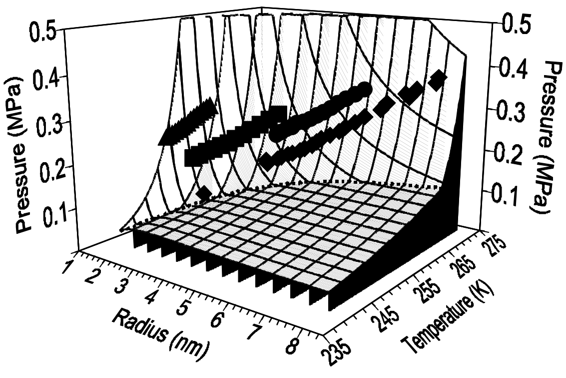

Fig. 4: (T_i,P_i,r_i) points determined from the data in Fig. 1 for propane hydrate in silica gels of nominal pore radii 2 (▲), 3 (■), 5 (●), or 7.5 (◆) nm, using eq. (1) to determine r_i.

As can be seen in Fig. 4, each experiment in which the temperature is raised incrementally and the equilibrium pressure measured at each temperature results in a curve on the (P,T,r) surface that may not be parallel to the r- axis, resulting in each pressure corresponding to a different pore size. Such considerations allow seemingly similar equilibrium pressures for different pore size distributions to be resolved. For example, the curves in Fig. 3 for the 7.5 and 5.0 nominal pore size silica gels for carbon dioxide hydrate seem to coincide for temperatures between 261 and 266 K. However, as shown in Fig. 5, the experimental paths on the $P(T,r)$ surface are clearly distinct. In Fig. 5 we have plotted $\ln(f)$ as a function of $1/T$ and $1/rT$ to reduce the surface to two planes (one each for the liquid and solid water equilibria), as suggested by Wilder et al (2002).

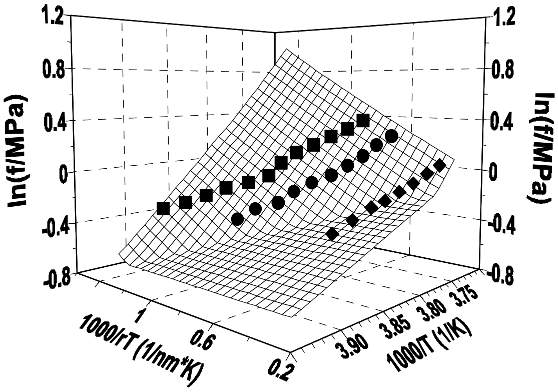

Fig. 5: $(1/T_i, 1/(r_iT_i), \ln(f_i))$ points determined from some of the experimental data in Fig. 3 for CO_2 hydrate in silica gels of nominal pore radii 3 (■), 5 (●), or 7.5 (◆) nm, using eq. (1) to determine r_i. Also shown is a portion of the complete $\ln(f)$ surface.

Once the experimental *P-T* data have been used to calculate the effective pore sizes, these data can then be use to calculate the volume of the pores from which hydrate decomposed to cause the pressure increase from P_i (at temperature T_i) to pressure P_{i+1} (at temperature T_{i+1}) (see Wilder et al, 2001 for details). Using the calculated amounts of gas released, as well as the pore size range the gas was released from, one can reconstruct a pore volume distribution. Such a set of reconstructions is presented in Figure 6 below. In Fig. 6, reconstructions are shown for the experimental data in Figs 1-3 for the nominal 7.5 nm pore size silica gel. The pore volumes have been normalized as discussed in Wilder et al (2001). Also shown in Fig. 6 are the pore volumes resulting from nitrogen desorption studies. As can be seen in Fig. 6, there is good agreement between the pore volumes reconstructed from experimental data both for the Structure I and Structure II hydrates. This agreement helps to validate this model for the interpretation of hydrate equilibria in porous media that have broad pore size distributions.

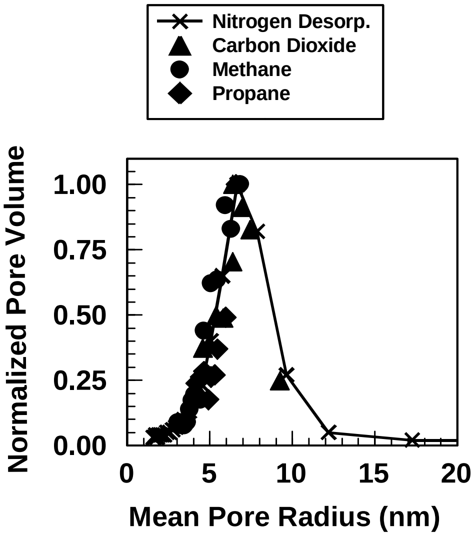

Fig. 6 Normalized pore volume distributions reconstructed from the experimental data in Figs. 1-3 for silica gels with nominal 7.5 nm pore radii. Also shown are the results based on the Autosorb-1 desorption isotherms (×).

The importance of the reconstruction in Fig. 6 lies not so much in the fact that it represents an indirect method to determine pore volume distributions, but that it represents a method to get information on how the hydrate was distributed in the porous medium. For example, as discussed elsewhere, the fact that a single scale factor can be used to reconstruct the pore volume distribution implies that the hydrate was equally distributed (Wilder et al, 2001a). While standard techniques such as nitrogen adsorption can be used to determine the pore volume distribution for a porous medium, this obviously gives no information concerning where in the medium the hydrate will form.

The quality of the reconstructed pore volumes shown in Fig. 6 also imply that the value for the surface tension between the hydrate and water is vely nearly that between ice and water (0.0267 J/m^2), as assumed by Henry et al (1999), Smith et al (2001a,b), and Wilder et al (2001a). If, for example, one were to use the value suggested by Uchida et al (1999) of 0.039 J/m^2, or that suggested by Clarke et al (1999) of 0.072 J/m^2, one arrives at reconstructed pore volume distributions such as those shown in Fig. 7, where the nominal 7.5 nm data have been used. Also shown in Fig. 7 for comparison purposes are the distributions obtained assuming our original value of 0.0267 J/m^2, as well as the distribution obtained from nitrogen adsorption. The results depicted in Fig. 7 suggest that 0.0267 J/m^2 is much closer to the true value of the surface tension between hydrate and water than are the other values shown in the Figure. See the results reported in Zhang et al (2002) for further support of this conclusion.

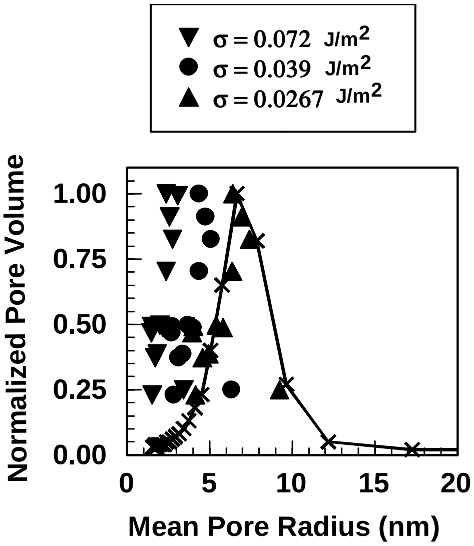

Fig. 7 Normalized pore volume distributions reconstructed from the experimental data for carbon dioxide hydrate in silica gels with nominal 7.5 nm pore radii using three different values for the hydrate – water surface tension (see text for details). Also shown are the results based on the Autosorb-1 desorption isotherms (×).

4 Conclusions

Handa and Stupin (1992) previously studied formation of propane and methane hydrates in silica gel with a nominal pore radius of 7.5 nm. Adequate study of the effects of capillary pressure on hydrate formation in small pores requires a series of experiments on samples with various nominal pore sizes. The failure of models presented in the literature (Clarke et al., 1999; Henry et al, 1999) to accurately predict the observed (Handa and

Stupin, 1992) equilibrium pressures implies that data for a range of pore sizes may be necessary for model validation studies. In this work we have shown data for a series of pore sizes for various hydrates, all of which clearly show capillary effects. In addition, both conceptual and mathematical models have been used to explain and interpret the experimental results. The results reported here demonstrate that (1) the correct interpretation of equilibrium data in porous media requires the consideration not only of the pressure and temperature, but of the pore size relevant to each individual equilibrium; (2) the modification of the van der Waals-Platteeuw equation to include capillary effects is applicable to hydrate formation in porous media; (3) the interfacial tension between hydrate and water is very closely approximated by that between ice and water for both sI and sII hydrates; (4) pore volume distributions reconstructed from hydrate data agree with those from nitrogen desorption, substantiating the model; and (5) the equilibrium fugacity (f) for hydrate formation in a porous medium can be written in terms of the pore radius (r) and the formation temperature (T) in the form $\ln(f) = a/T + b/r_i T_i + c$, where a, b, and c are compound dependent constants.

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