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The Effect of Pressure on Methane Hydration in Pure Water and Sodium Chloride Solutions

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Abstract

Traditionally, the effect of pressure on hydrate formation has been described using the Clausius-Clapeyron equation, which assumes that only vapor phase volume changes are significant. According to this assumption, equilibrium data for any hydrate former will fit to straight lines with equal slope on a plot of logarithmic pressure versus temperature. But both data and theory shows that this is not true at higher pressures.

In this research, equilibrium data of methane hydrate dissociation were measured up to pressures of 70 MPa and at 4 different concentrations of NaCl. These measurements were done using a new experimental method. Raman spectroscopy was used to detect the presence and determine the structure of hydrates. The data show significant deviations from linear Clausius-Clapeyron behavior.

Calculations have been done on literature data for methane hydrate and new data. Both the Clapeyron relation and van der Waals & Platteeuw hydrate theory has been used. Both models represent the data well, but show interesting minor deviations at high salt concentration.

Keywords: Data, solid-fluid equilibria, methane hydrate, sodium chloride

1. Introduction

Clathrate hydrates, or gas hydrates, are crystalline inclusion compounds formed in mixtures of water and hydrocarbon molecules. These solids consist of a hydrogen-bonded lattice of water molecules. This lattice contains open spaces, or cavities, which will collapse, unless they are stabilized by small ($< 9 \text{ \AA}$ diameter) apolar molecules. Of main practical interest are hydrates that are stabilized by the lower alkanes.

The formation of gas hydrates is one of the main concerns of flow assurance in natural gas transportation pipelines. Hydrate risks are aggravated by low temperatures and higher pressures, exactly the conditions that occur in deepwater exploration of natural gas. Since exploration is generally moving to greater depths, thermodynamic data and models are needed that are accurate up to at least 70 or even 100 MPa.

There are some hydrate data available in literature at high pressures, but especially for hydrates in the presence of the most common inhibitors (methanol, sodium chloride), data are scarce or non-existent. To meet the need for new data, we have started a research program to measure high pressure data and adapt the current hydrate model to the new data.

Data will be measured on methane hydrates, in the presence of various concentrations of sodium chloride (up to 8 mol%) and methanol (up to 40 wt%). The data taken are standard phase equilibria data, where the temperature and pressure condition at which the last hydrate crystal disappears is taken as the equilibrium point. However, a new experimental technique is used for hydrate detection, Raman spectroscopy. The main advantage of this technique is that structure of the hydrate phase present can be measured alongside the phase equilibria points. Although this experimental technique has been used

successfully by other researchers [1] [2], we compare our data with independent low pressure data to ensure accuracy. Data obtained for the system water + methane + NaCl are reported in this article.

The data can be modeled using the classical theory for clathrate hydrates, derived by van der Waals and Platteeuw [3]. Their expression for the hydrate chemical potential can be equated to the water chemical potential, for which Holder derived an expression [4]. An adapted version of this equation by Holder is used to account for the compressibility of phases, which is significant at higher pressures.

The idea to use the Clapeyron equation to understand the data we measure, originated from the fact that non-linearity in the slope of the methane hydrate equilibrium curve was found back in the equilibrium curves for hydrates in the presence of salts. By carefully accounting for the enthalpy and volume changes upon hydrate dissociation on a per unit cell basis, these slope changes are mimicked by our models. But the modeling using the Clapeyron equation also showed fascinating differences in behavior at very high pressures, depending on the equation of state used to describe the methane gas phase.

2. Experimental Method

Chemicals used

The chemicals used were as follows. Ultra high purity methane (>0.9999) supplied by Air Liquide was used together with distilled water (Nalgene) and sodium chloride (>99%, Fisher). Different salt solutions were prepared from water and sodium chloride, using a Mettler balance (0.0001 g precision).

Experimental apparatus

A schematic of the experimental setup used in our experiments is given in Figure 1. The heart of the apparatus is a brass high pressure cell with a sapphire glass window. This cell has an inner volume of approximately 1 cm^3 and is rated up to pressures of 70 MPa. The cell has an in- and outlet for cooling fluid, which can be circulated through the block itself. For cooling fluid a mixture of water and methanol was used. A Haake A80 temperature bath was used to control the temperature of the cooling fluid. The temperature was measured using a thermocouple that was calibrated against a Fisher mercury thermometer.

The pressure in the cell is controlled by pumping a certain amount of methane into the cell using a Haskel gas booster pump. The pressure is measured by a Heise pressure transducer. Both pressure and temperature readings can be collected in real time by a data acquisition system. The errors in temperature and pressure measurements are smaller than 0.2 K and 1 % respectively.

Experimental procedure

At the start of an experiment, the high pressure cell is charged with a salt solution of known composition and a certain amount of methane. The cell is then mounted on a XY translation stage. Hydrates are formed by decreasing the temperature. Hydrates usually form as a very thin crust at the liquid + vapor interface.

Once hydrates are formed, the presence of hydrates can be detected by obtaining a Raman spectrum of the interface. The Raman spectrometer used in this research is a

Renishaw fiber optic based system, using a 2400 grooves/mm grating. A 30 mW Argon ion (514.5 nm) air-cooled laser is used as an excitation source. The laser is focused on the interface by adjusting the position of the equilibrium cell with respect to a probe head that emits the laser beam. Standard neon emission lines are used for the calibration of the spectrometer.

The actual experiment is a slow heating of the high pressure cell, while temperature, pressure and Raman spectra of the interface are collected real time. A typical heating rate is 0.1 K per 2 minutes or slower. Dissociation of the hydrates present at the interface is characterized by a disappearance of the hydrate Raman signal. The temperature at which the last recognizable hydrate Raman spectrum was measured, is taken as the equilibrium point. An example of the accumulated hydrate spectra collected from an equilibrium experiment is given in Figure 2. The stray peak on the right side is a cosmic ray.

As can be seen from the figure, at the start of the experiment a typical Raman methane signal shows the presence of hydrates. During the experiment, the hydrate signal deteriorates into the signal for methane dissolved in water. The phases corresponding to the signals can easily be found by comparison with earlier measured Raman spectra [5].

3. Experimental Results

Methane hydrate data phase equilibrium curves have been measured for pure water and sodium chloride solutions of 2, 3.61, 6 and 8 mol% of sodium chloride relative to water. The equilibrium curves are tabulated in Table 1 and shown in Figure 3.

The data measured for methane hydrate in pure water compare very well with data reported in the literature [6]. Of course, there are no data available in the literature at high pressures for the different concentrations of sodium chloride. However, low pressure data have been measured for this system by de Roo et al. [7] up to pressures of 10 MPa. Our hydrate equilibrium data below 10 MPa compare on average within 0.2 K with the correlation given by de Roo et al.

Some of the data have been measured by dropping the pressure in small steps instead of increasing the temperature. These data points were not noticeably different from the data obtained by slowly increasing the temperature. All hydrate spectra observed were characteristic for sI methane hydrates.

4. Modeling

A simple combination of three expressions, one for each consecutive phase, has been used to model the hydrate phase equilibrium curves measured in this work. Classical van der Waals & Platteeuw theory has been used to model the chemical potential of the hydrate phase. A modified form of the expression developed by Holder combined with Pitzer's description of water activity has been used to describe the chemical potential of the water phase [8]. The SRK equation of state models the gas phase, which is assumed to consist only of pure methane [9]. These models have been combined to predict the data, using no further adjustable parameters.

Van der Waals and Platteeuw were able to find an expression for the chemical potential difference. This quantity is defined as chemical potential of water in a theoretical

empty hydrate lattice minus the chemical potential of water in a real hydrate. Assuming rigidity of a hydrate lattice, this is only a function of the fractional occupancy of the hydrate cavities with guest molecules (Eq. 1). The occupancy of the hydrate lattice is a function of the fugacity of the occupying guest and a Langmuir constant that quantifies the interaction between the guest molecule and the water molecules in the cavity wall (Eq. 2).

$$\Delta m_w^H = -R_c \cdot T \cdot \sum_i n_i \cdot \ln \left(1 - \sum_k q_{ki} \right) \quad (1)$$

$$q_{ki} = \frac{C_{ki} \cdot f_k}{1 + \sum_j C_{ji} \cdot f_j} \quad (2)$$

If one assumes that the hydrate cavities are approximately spherical, the Langmuir constants can be evaluated from integrating a spherical Kihara potential. Details of this integration have been described extensively in the literature, see for example Mehta and Sloan [10].

Hydrate equilibrium occurs when the chemical potential difference in the hydrate phase equals that in the water-rich liquid phase. The modified expression that we use in this work is given in Eq. 3. Notice that the new term in the expression is the compressibility difference in the pressure integral ($\Delta \kappa_w^L$), which can be neglected at low pressures but is significant at higher pressures. This compressibility difference can be easily calculated by comparing the compressibility of water, found from a steam table and the compressibility of hydrate, which is small for a hydrate with both small and large cages occupied.

$$\frac{\Delta m_w^L}{R_c \cdot T} = \frac{\Delta m_w^0}{R_c \cdot T_0} - \int_{T_0}^T \frac{\Delta H_w^L}{R_c \cdot T^2} dT + \int_0^P \frac{\Delta V_w^L + \Delta \kappa_w^L}{R_c \cdot T} dP - \ln(\mathbf{g}_w \cdot x_w) \quad (3)$$

The activity of water (γ_w) can be calculated for water + sodium chloride mixtures with a Pitzer expression given in Eq. 4 and Eq 5:

$$\ln(\mathbf{g}) = -\mathbf{n} \cdot \left(1 - A_f(T) \cdot \frac{\sqrt{I}}{1 + 1.1 \cdot \sqrt{I}} + I \cdot [\mathbf{b}_0 + \mathbf{b}_1 \cdot e^{-2\sqrt{I}} + \mathbf{b}_2 \cdot I^2] \right) \quad (4)$$

$$A_f = 0.1342 \cdot (4.173 - 0.1481 \cdot \sqrt{T} + 1.519 \cdot 10^{-5} \cdot T^2 - 1.802 \cdot 10^{-8} \cdot T^3 + 9.382 \cdot 10^{-10} \cdot T^{3.5}) \quad (5)$$

In equations 4 and 5, water activity is only a function of temperature and composition. In reality, there is also a slight pressure dependency of the water activity. However, the original Pitzer correlations do not include a pressure dependency. This may be a suggestion for future improvement of the model.

The values of the parameters used have been included in Table 2. The modeling results are also shown in Figure 3. As can be seen from Figure 3, the model reproduces the data very accurately, except at high concentrations of salt and high pressures. The average deviation between the calculated and measured pressures is smaller than 5 % for every data set, the maximum error being 11 %.

5. Modeling using the Clapeyron equation

It is generally assumed that hydrate equilibrium curves approximate straight lines in a $\ln(P)$ versus $1/T$ plot, as would be expected from a Clausius-Clapeyron relation, with a constant heat of dissociation (Eq. 6).

$$\frac{d \ln(P)}{d(1/T)} = - \frac{\Delta H}{R_c} \quad (6)$$

However, it has been shown already that hydrate equilibrium curves can be far from linear on a $\ln(P)$ vs. $1/T$ plot in the vicinity of the critical point of the guest molecule [11]. But even the methane hydrate equilibrium curve, more than 100 K removed from the critical point of methane, shows non-linearity at pressures above 20 MPa. These equilibrium curve slope changes can be quantified by comparing the real equilibrium curve with an extension of a Clausius-Clapeyron equation fitted to all methane equilibrium data up to 20 MPa (Eq 7):

$$\ln[P_{reg} (MPa)] = \frac{-8375.06}{T(K)} + 31.5775 \quad (7)$$

The data for methane hydrate mentioned in the literature [6] can be compared with this equation and a dimensionless deviation from linear behavior (called η) can be calculated using Eq. 8. The same procedure can be followed for our data measured with salt present in the solution, since a low pressure equation similar to Eq. 7 has been given by de Roo et al. [7].

$$h = \frac{P_{data} - P_{reg}}{P_{reg}} \quad (8)$$

A plot of the dimensionless linear deviation η versus temperature is given as Figure 4. It is clear that the slope changes of the methane hydrate curve in pure water are copied for the various salt solutions. These slope changes do not indicate structural transitions of the hydrate lattice, since we know from our spectroscopic data that methane forms sI hydrates at least up to 70 MPa. In fact, these slope changes mainly indicate high pressure non-idealities in the gas phase, which can actually be modeled using a Clapeyron equation.

The Clapeyron equation expresses the slope of an equilibrium curve as a function of the volume and enthalpy effects related with the phase change. If exact relations for the volume and enthalpy effect are known, it should give a thermodynamically rigorous expression for the slope of the equilibrium curve in question. For methane hydrate, we derived such an equation by expressing the volume and enthalpy effects on a hydrate unit cell basis.

$$\frac{dP_{H \rightarrow L+V}}{dT} = \frac{\Delta H_{H \rightarrow L+V}}{T \cdot \Delta V_{H \rightarrow L+V}} \quad (9)$$

$$\Delta H_{H \rightarrow L+V} = H_H - 46 \cdot H_L - \left(2 \cdot \mathbf{q}_s + 6 \cdot \mathbf{q}_l - \frac{46 \cdot x_m}{1 - x_m} \right) \cdot H_V \quad (10)$$

$$\Delta V_{H \rightarrow L+V} = a(P, T)^3 \cdot N_A - 46 \cdot V_L - \left(2 \cdot \mathbf{q}_s + 6 \cdot \mathbf{q}_l - \frac{46 \cdot x_m}{1 - x_m} \right) \cdot V_V \quad (11)$$

The enthalpy and molar volume of the liquid water phase have been regressed from the steam tables [12]. The methane enthalpy and molar volume has been calculated from the SRK equation of state. The solubility of methane can be found from a Krichevsky-Kasarnovsky equation [13]. The lattice parameter for sI hydrates is known and the enthalpy of the hydrate is found from the heat of dissociation [14].

The Clapeyron equation has been used to calculate the data collected in this work. Since the slope of the equilibrium line is known as a function of P and T, the entire equilibrium line can be calculated from one data point. For pure water, the quadruple point I + sI + Lw + V has been taken as an initial point. For the various salt solutions, the correlation by de Roo et al. has been used to obtain an initial low pressure point.

Calculations have been done using a temperature step of 0.01 K. The results of these predictions are given in Figure 5.

The Clapeyron equation appears to predict the data fairly accurately. Average error on pressure is below 4 %, with a maximum of 14 %. An unusual and unexpected result is that the deviations between the two models are different at high pressures and salt concentration. The Clapeyron equation predicts equilibrium pressures that are too high, while the van der Waals model predicts equilibrium pressures that are too low. The deviation of the Clapeyron equation at high salt concentration may be caused by the fact that the pure water enthalpy is still used. Using partial water properties for the water phase may be a significant improvement, but would make the equation more complex.

6. Conclusions

Structure I hydrate equilibrium data for the system water + salt + methane have been measured up to 70 MPa using Raman spectroscopy. The data comply within 0.2 K with low pressure data available from literature. The data can satisfactorily be modeled using a combination of van der Waals and Platteeuw theory with Pitzer's theory for water activity. The slope of the measured hydrate equilibrium curves can be modeled with a Clapeyron equation, if the volume and enthalpy changes of dissociation are known. For both models, no additional adjustable parameters are needed to obtain pressure predictions that are on average within 5 % of the measured data.

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Nomenclature

a	Hydrate unit cell lattice parameter	(m)
C_{ki}	Langmuir constant of type k hydrate former in type i cavity (Pa^{-1})	
f	Fugacity	(Pa)

ΔH_w^L	Enthalpy difference between empty lattice and water	(J mol ⁻¹)
$\Delta H_{H \rightarrow L+V}$	Heat effect upon dissociation	(J mol _{unitcell} ⁻¹)
I	Ionic strength	(mol kg ⁻¹)
N _A	Avogadro's number	
P	Pressure	(Pa)
R	Radius of hydrate cavity	(Å)
R _c	Universal gas constant	(J mol ⁻¹ K ⁻¹)
T	Temperature	(K)
ΔV_w^L	Volume difference between empty lattice and water	(m ³ mol ⁻¹)
$\Delta H_{H \rightarrow L+V}$	Volume effect upon dissociation	(m ³ mol _{unitcell} ⁻¹)
x _k	Liquid phase mole fraction of component k	
β	Pitzer coefficients	
γ	Activity coefficient	
η	Dimensionless deviation from Clausius-Clapeyron equation	
θ _{ki}	Fractional occupancy of type i cavity by type k molecules	
$\Delta \kappa_w^L$	Compressibility difference between empty lattice and water	(m ³ mol ⁻¹ Pa ⁻¹)
v	Salt stoichiometry	
v _i	Number of cavity type I per water molecule	
Δμ	Chemical potential difference	(J mol ⁻¹)
Δμ ⁰	Reference chemical potential difference	(J mol ⁻¹)

Table 1. Measured hydrate equilibrium data for the system water + methane + NaCl.

0 mol%		2.001 mol%		3.611 mol%	
T(K)	P(MPa)	T(K)	P(MPa)	T(K)	P(MPa)
291.86	20.19	280.66	6.60	279.16	7.51
293.08	22.91	286.00	13.71	284.53	14.07
293.46	24.23	289.42	21.38	287.50	23.38
295.08	30.46	291.71	28.18	288.30	23.88
295.94	34.28	293.42	35.94	289.23	27.19
297.48	43.46	293.51	34.84	290.55	34.69
297.58	42.35	295.62	45.52	292.15	41.85
298.24	45.64	296.30	48.75	293.37	49.00
298.68	50.45	297.42	56.20	294.58	57.63
301.67	65.97	298.42	63.25	295.47	64.60
302.70	68.72	299.06	67.81	296.03	71.56
303.48	72.26				

5.994 mol%		8.014 mol%	
T(K)	P(MPa)	T(K)	P(MPa)
274.40	7.92	270.66	7.85
280.25	14.32	275.22	14.94
282.33	20.74	278.04	22.98
284.67	29.12	279.20	28.18
286.23	35.93	281.29	37.86
287.47	42.93	282.39	42.26
288.42	49.53	283.49	50.57
289.21	56.47	284.36	58.85
290.37	64.14	284.92	64.03
291.00	70.56	285.76	71.30

Mole percentages are moles sodium chloride with respect to water.

Table 2. Values of parameters used

Parameter	Value	Unit	Comments
$\Delta\mu_w^0$	1287	J mol ⁻¹	
ΔH_w^0	-5081.35	J mol ⁻¹	
$\Delta C_{p_w}^0$	-38.12	J mol ⁻¹ K ⁻¹	
B	0.141	J mol ⁻¹ K ⁻²	
ΔV_w^L	4.6 e-6	m ³ mol ⁻¹	
T ₀	273.15	K	
R	3.95 ; 4.33	Å	Small and large cage respectively
$\Delta\kappa_w^L$	6.695 e-15	m ³ mol ⁻¹ Pa ⁻¹	Compressibility difference
a	0.3834	Å	Kihara parameter
σ	3.102	Å	Kihara parameter
ϵ/k	161.368	K	Kihara parameter

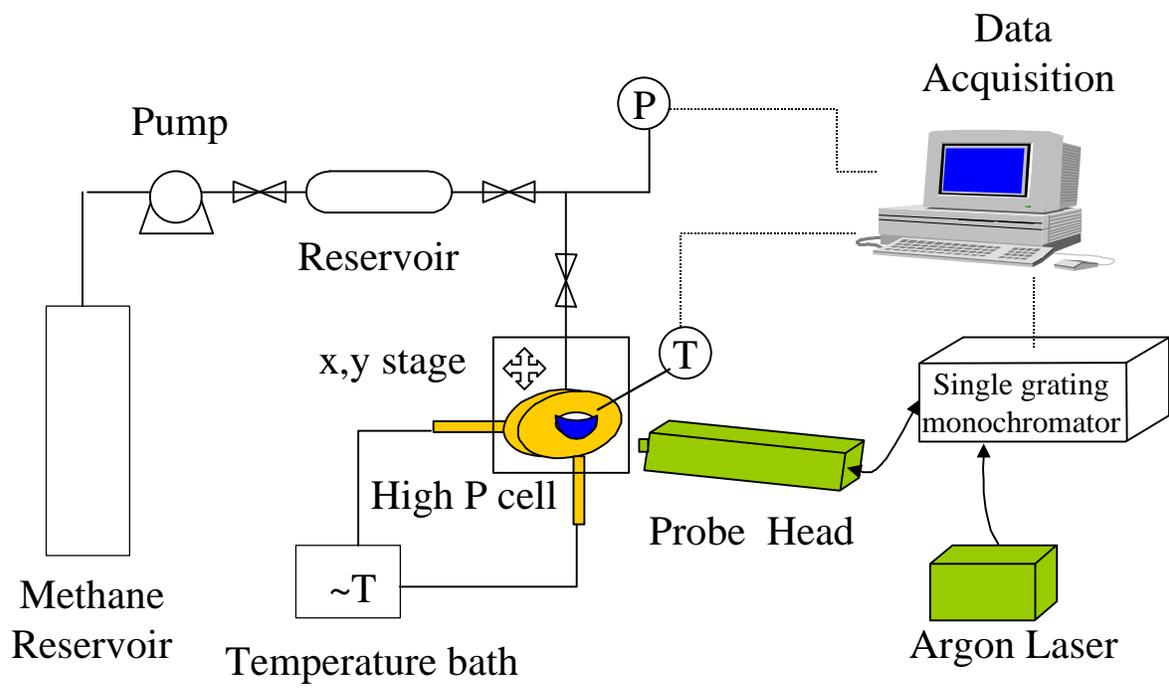


Figure 1. Experimental apparatus used in phase equilibria experiments

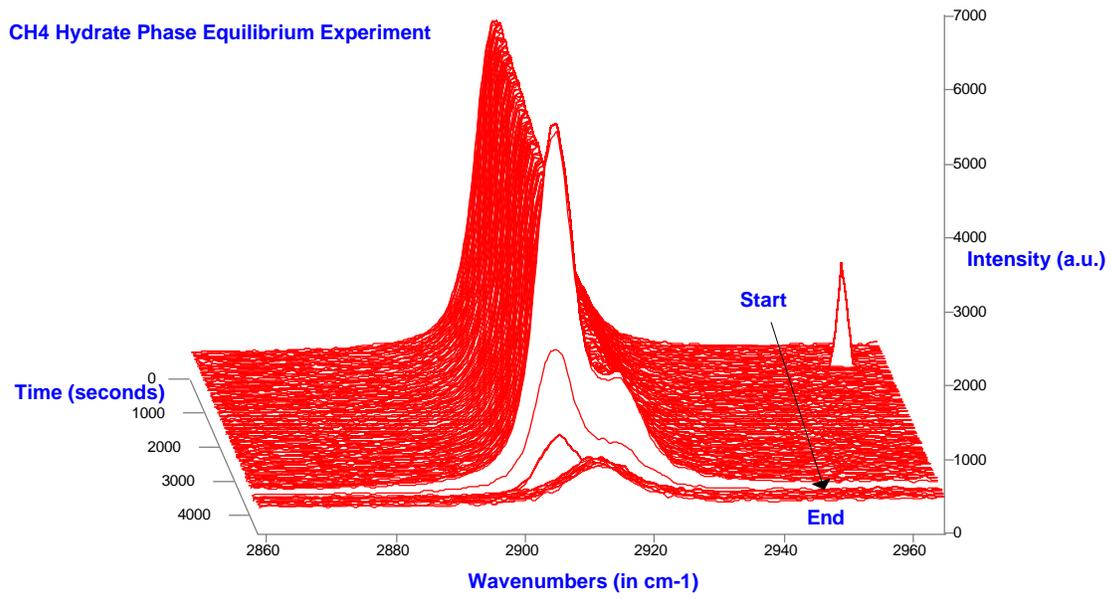


Figure 2. Example of Raman spectra used to determine hydrate dissociation point

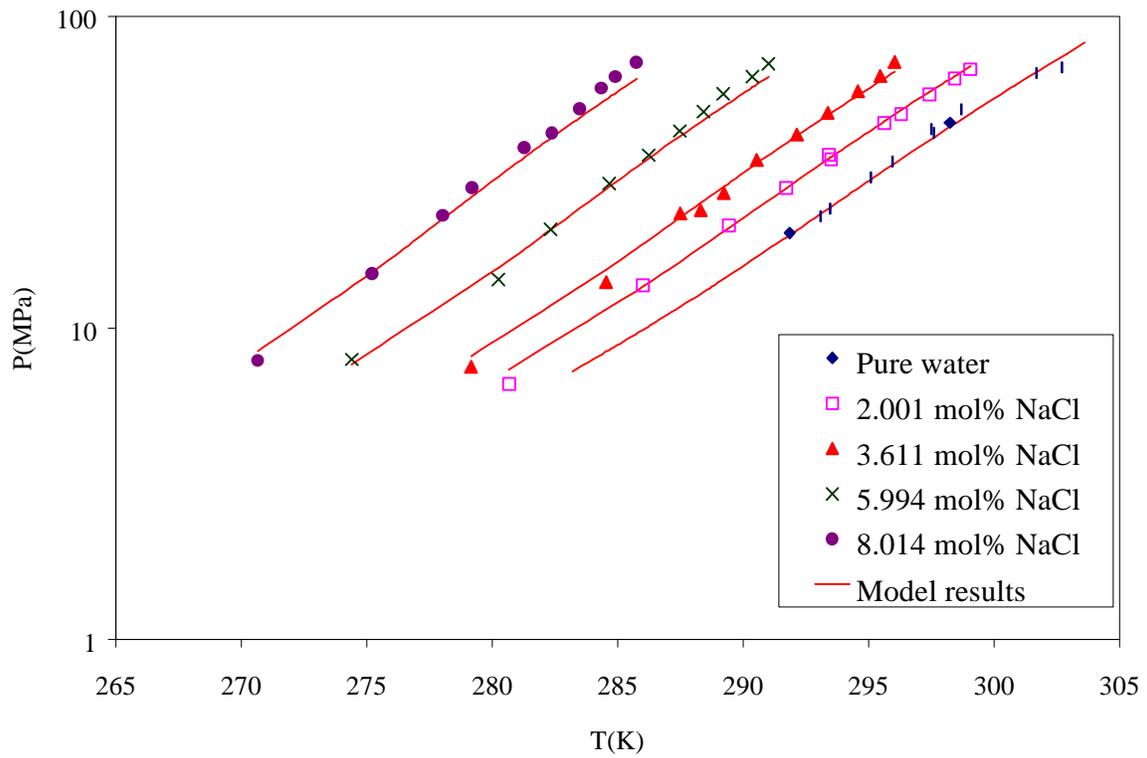


Figure 3. All hydrate data collected and classical model results

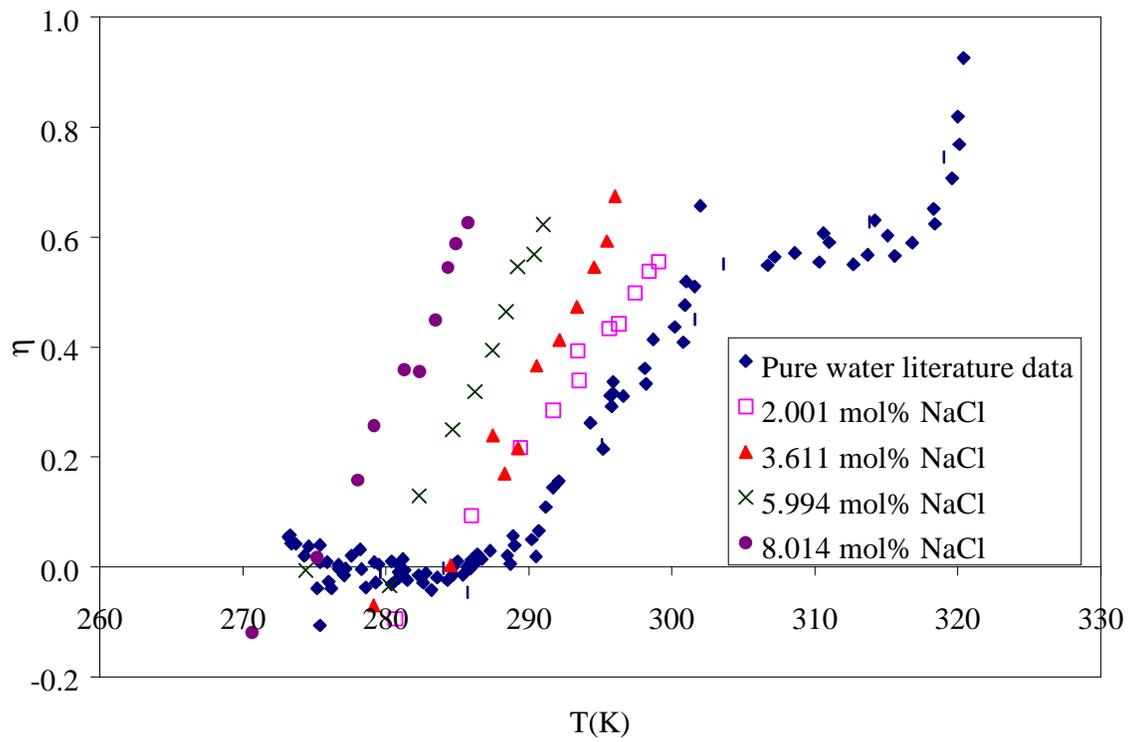


Figure 4. Dimensionless linear slope deviation for methane hydrate equilibrium curves

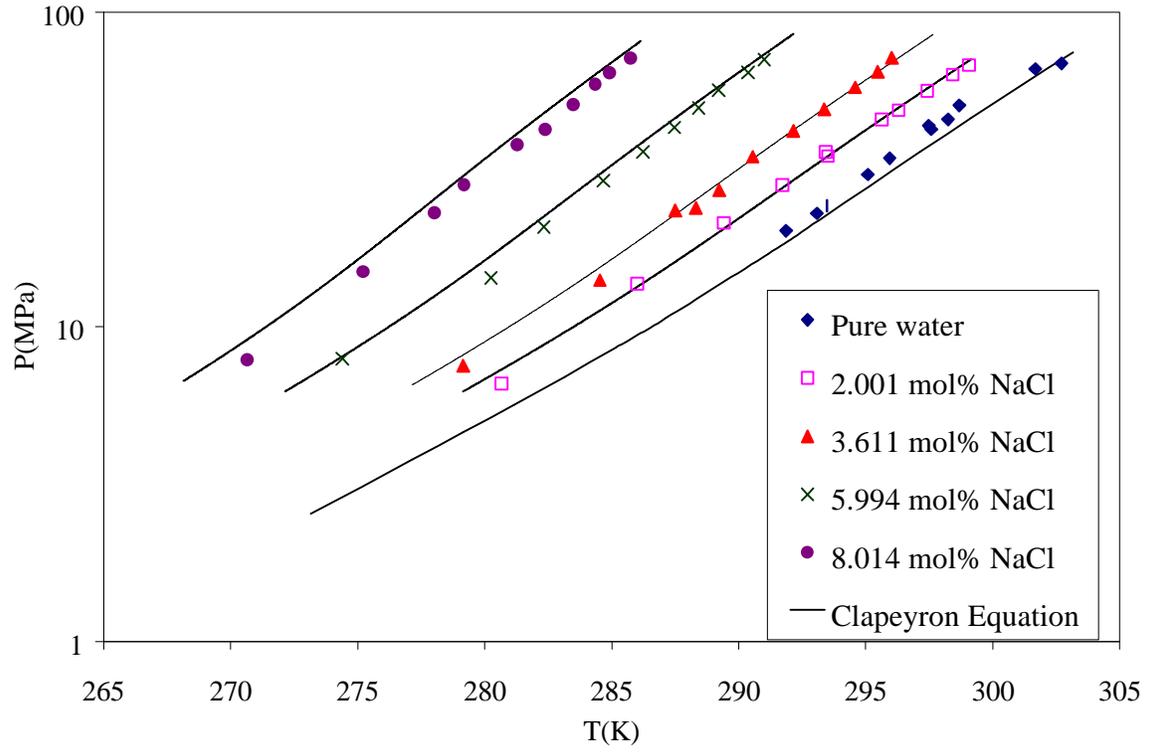


Figure 5. Modeling results from Clapeyron equation compared to hydrate data collected