COBEM2015

ABCM Associação Brasileira de Engenharia e Ciências Mecânicas

23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

EXPERIMENTAL AND MODELING OF CARBON DIOXIDE HYDRATE PHASE EQUILIBRIUM IN THE PRESENCE OF THERMODYNAMIC INHIBITORS

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Abstract. *Hydrates are crystalline compounds formed by occlusion of gas or liquid of low molecular weight inside a crystalline structure consisting of water molecules. Hydrates can block oil and gas lines in petroleum industry, reducing process efficiency, damaging equipments and risking safety operation. It is well-know that carbon dioxide (CO_2) is one of the most common non-hydrocarbon gases found in petroleum reservoirs. In addition to this, most of the pre-salt fields in Brazil hold a significant rate of CO_2. Therefore understanding the phase equilibrium behavior of CO_2 hydrates is fundamental. This study presents phase equilibrium curves of CO_2 hydrates with ethanol inhibitor. The parameter of main interest is the equilibrium pressure, at which hydrates form at a given temperature and inhibitor concentration. An equilibrium cell was used in order to obtain these curves by means of the static synthetic method and isothermal procedure. The operating temperature varied from 275.65 up to 281.65 K and pressure from 1 up to 5 MPa. A statistical thermodynamic approach with the Cubic Plus Association equation of state, has been applied to model this phase equilibrium. Hydrate-forming conditions were modeled by the van der Waals-Platteeuw theory. The model was validated against experimental hydrate equilibrium data. Satisfactory agreement was obtained between the model and experiments; average absolute deviations of the model were 6.6% (without inhibitor) and 15.5% (with inhibitor).*

Keywords: *Hydrates, Inhibitor, Prediction, Experimental, Modeling*

1. INTRODUCTION

Gas hydrates belongs to a family of nonstoichiometric compounds in which hydrogen-bonded water molecules are arranged in an icelike framework, forming polyhedral cavities occupied by “guest ”molecules (*e.g.*, methane, ethane, propane, carbon dioxide, *etc*.).

CO_2 hydrate crystallizes in one of the two cubic hydrate structures (structure I), in which the unit cell consists of 46 H_2O molecules and up to 8 CO_2 molecules occupying both small (pentagonal dodecahedral) and large (tetrakaidecahedral) cavities in a ratio of 1:3. CO_2 hydrate is stable over a range of elevated pressure and low-temperature conditions (Sloan and Koh, 2008).

Hydrates are an extremely relevant issue in flow assurance. Indeed, hydrates can severely affect drilling and oil well production operations by either impairing or completely bringing those operations to a complete halt. Hydrate formation causes interruption and impairment in the production due to the time spent on cleaning of pipelines. Besides, the elimination of hydrates presents high levels of operational risks.

In situations where hydrates are likely to form, several methods are available to prevent or suppress their occurrence. In some cases, simple manipulation of the system temperature and pressure may be adequate to avoid hydrates. Water removal or dehydration of the process is very effective. However, in some cases it may not be cost effective to implement one of these methods. For those areas, the injection of thermodynamic inhibitors, such as alcohols and salts, is typically the favorite choice due to their inherent properties of hydrate suppression.

With the beginning of oil exploration from the brazilian Pre-salt reservoirs, the study of the phase behavior of CO_2 + H_2O systems gained visibility in petroleum industry, since high concentrations of carbon dioxide in the composition of the oil and gas in that region were predicted. According to Melo *et al.* (2011), concentrations from 8 up to 12% of CO_2

were found in Tupi field concession in Brazil. Thus, these facts justify the relevance of studying the phase equilibrium inherent to the formation of CO_2 hydrates.

Despite the existing literature on CO_2 hydrate phase equilibrium and physical properties (Deaton and Frost, 1946; Unruh and Katz, 1949; Ng and Robinson, 1983; Adisasmito *et al.*, 1991; Ohgaki *et al.*, 1993; Fan and Guo, 1999; Wendland *et al.*, 1999; Fan *et al.*, 2000; Hachikubo *et al.*, 2002; Zhang, 2003; Mohammadi *et al.*, 2005) there is a lack of studies dealing specifically with CO_2 hydrate phase equilibrium in the presence of ethanol inhibitor. Ethanol acts by lowering the activity of the water, and generally shifts the equilibrium lines for hydrate formation in the phase diagram to lower temperatures and higher pressures.

This paper presents a modeling and experimental study of the phase equilibrium for CO_2 + H_2O system, with and without inhibitor, accomplished in an equilibrium cell by the static-synthetic method and isothermal procedure. Experimental results are presented for a temperature range from 275.65 up to 281.65 K and for a pressure range from 1 up to 5 MPa. Additionally, a model for the three-phase equilibrium (hydrate, liquid and vapor phases) has been numerically implemented and confronted to the experimental and literature data. The applied model incorporates the Cubic Plus Association (CPA) (Kontogeorgis *et al.*, 1996) equation of state for the fluid phase description and the van der Waals-Platteeuw hydrate model (van der Waals and Platteeuw, 1959) for the solid (hydrate) phase.

2. THERMODYNAMIC MODELING

The equilibrium condition for a multiphase thermodynamic system is the equality between the pressure, the temperature and the chemical potential for each substance in the different phases (Smith *et al.*, 2004). In the case of the chemical equilibrium between a hydrate (solid), a liquid and a vapor phase, we have

$$\hat{\mu}_i^H(P,T,w_1,w_2,...,w_n) = \hat{\mu}_i^L(P,T,x_1,x_2,...,x_n) = \hat{\mu}_i^V(P,T,y_1,y_2,...,y_n), \tag{1}$$

where $\hat{\mu}$ is the chemical potential, P is the pressure, T is the temperature, the labels H, L and V stands for the hydrate, liquid and vapor phases, and the quantities w_i, x_i and y_i are the mole fractions of component i in each of the three phases. The i index runs over all the n components ($i = 1, 2, ..., n$). In this work, the system composed by water, carbon dioxide and ethanol have been studied (i.e. $n = 3$). In the inhibition-free case (no ethanol), as a consequence of the Gibbs Phase Rule (Smith *et al.*, 2004), we may only specify one thermodynamic function to completely determine the state of the system in the hydrate-liquid-vapor (three phase) equilibrium. Consequently, it is possible to find an equilibrium pressure value for each temperature. This is possible via the equality of the chemical potential of water:

$$\hat{\mu}_w^H(P,T) = \hat{\mu}_w^L(P,T) = \hat{\mu}_w^V(P,T). \tag{2}$$

The dependence of each term of Eq. (2) on pressure and temperature is given, in this work, by a combination of the CPA Equation of State (Kontogeorgis *et al.*, 1996) and the Van der Waals-Platteeuw (VdWP) theory (van der Waals and Platteeuw, 1959).

2.1 The CPA Equation of state

The Cubic Plus Association (CPA) equation of state was initially proposed by Kontogeorgis *et al.* (1996). It can be written as

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln(g)}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}). \tag{3}$$

It can be seen that the right hand side of Eq. (3) above is a sum of three terms. The first two are the contribution from the cubic part, identical to the Soave-Redlich-Kwong (SRK) equation of state. There are two parameters in the SRK equation, the energy parameter a and the co-volume parameter b. These are given by

$$a = \sum_{i,j}\sqrt{a_i(T)a_j(T)}(1 - k_{ij}), \tag{4}$$

with

$$a_i = a_0\left[1 + c_1(1 - \sqrt{T/T_c})\right]^2, \tag{5}$$

and:

$$b = \sum_i x_i b_i. \tag{6}$$

In Equations (4), (5) and (6), there are additional one components parameters a_0, c_1 and b_i and the binary interaction parameters k_{ij} (T_c is the critical temperature). Their values are obtained from liquid-vapor equilibrium curves fitting. For this work, they were taken from Tsivintzellis *et al.* (2011) and are displayed in Table 1.

Table 1. Physical parameters of CPA.

Substance	Water	Carbon dioxide	Ethanol
a_0 (m^6 Pa mol^{-2})	1.2277 E-1	3.5079 E-1	8.6716 E-1
c_1 (-)	0.6736	0.7602	0.7369
b (m^3 mol^{-1})	0.0145 E-3	0.0272E-3	0.0491E-3

The third term in the CPA equation is the association contribution, which depends on the interaction energy between hydrogen bond forming molecules. It involves the molar density ρ, the molar fractions x_i, the radial distribution function g and the quantities X_{A_i}. The central quantity in this formulation is X_{A_i}, the fraction of molecules A not bonded at site i. This fraction depends on the geometry and the distribution of charge of the molecule, and some simplifying association schemes have been proposed to calculate it, with excellent results obtained (Kontogeorgis *et al.*, 2006). Following the nomenclature presented, for instance, in Kontogeorgis and Folas (2010), in this work, it has been adopted the 4C-scheme for water and the 2B-scheme for ethanol. For carbon dioxide, it was assumed that it only cross-associates (with water and ethanol), with two electron accepting sites forming bonds with it (Tsivintzellis *et al.*, 2011).

The expression used to compute the X_{A_i} values is the implicit set of equations given by

$$X_{A_i} = \frac{1}{1 + \frac{1}{V_m} \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}}. \tag{7}$$

The sum on the denominator of Eq. (7) is over all sites B_j that form bonds with site A_i. The determinant quantity is $\Delta^{A_i B_j}$, which is related to the interaction energy $\epsilon^{A_i B_j}$ by

$$\Delta^{A_i B_j} = g(V_m) \left[\exp\left(\frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j}. \tag{8}$$

Again, the parameters $\epsilon^{A_i B_j}$, $\beta^{A_i B_j}$ and $b_{ij} = \frac{1}{2} = (b_i + b_j)$ were taken from previous studies (Tsivintzellis *et al.*, 2011) and are shown in Tables 2 and 3.

Table 2. Energy parameters ($\epsilon^{A_i B_j}$) of CPA (Pa m^3 mol^{-1}).

Substance	Water	Carbon dioxide	Ethanol
Water	166.55 E+2	83.28 E+2	190.935 E+2
Carbon dioxide	83.28 E+2	0	107.66 E+2
Ethanol	190.935 E+2	107.66 E+2	215.32 E+2

Table 3. Volume interaction parameters ($\beta^{A_i B_j}$) of CPA.

Substance	Water	Carbon dioxide	Ethanol
Water	0.0692	0.0235	0.0235
Carbon dioxide	0.0911	0	0.0236
Ethanol	0.0235	0.0236	0.008

One reason for using the CPA equation in this model is the fact that the molecules of the three components studied (water, carbon dioxide and ethanol) can form hydrogen bonds between themselves and this influences the hydrate equilibrium conditions. This effect is accounted in the fugacity of the carbon dioxide in the gas phase, in the solubility of gas in the liquid phase and in the activity of water in the liquid phase. These three quantities (calculated from CPA) are important in our model as will be shown next.

2.2 The Van der Waals-Platteuw (VdWP) Theory

The VdWP theory computes the change in the chemical potential of water as a result of gas occlusion by the crystal structure. One can write this change as

$$\Delta\mu_w^{\beta-H} = \hat{\mu}_w^H(P,T,w_1,w_2) - \hat{\mu}_w^\beta(P,T) \tag{9}$$

Here, β is hypothetical empty water crystal structure with no gas molecules, used for calculation convenience as a reference state. According to the VdWP theory, it is possible to write the variation as a result of the occlusion of gas molecules as

$$\Delta\mu_w^{\beta-H} = RT\sum_k v_k \ln\left(1-\sum_i Y_{ik}\right), \tag{10}$$

where v_i is the number of cages of type i per water molecule in a unit cell of the crystal and Y_{ik} is the probability that a molecule of species i is occluded in a cage of type k. This probability is given by

$$Y_{ik} = \frac{C_{ik}f_i}{1+\sum_i C_{ik}f_i}. \tag{11}$$

In this equation, f_i is the fugacity of species i in the gas phase and the constants C_{ki} are the so called Langmuir constants, a terminology derived from an analogy with the theory of gas adsorption by a solid surface (Sloan and Koh, 2008). Following van der Waals and Platteeuw (1959), these can be computed as

$$C_{ik} = \frac{4\pi}{kT}\int_0^{R_k-a_i} \exp(-w_{ik}(r)/kT)r^2\mathrm{d}r. \tag{12}$$

In Equation (12), k is the Boltzmann constant, R_k is an average radius of cage k (bounded by the water molecules), a_i is the radius of gas molecule of species i and $w(r)$ is the potential energy of the interaction between the gas and the water molecules as a function of the distance between the center of the cage and the position of the molecule of gas. Here, it has been assumed a spherically symmetrical interaction potential, that can be calculated, in our model, using the Kihara potential (Sloan and Koh, 2008):

$$w_{ik}(r) = 2z\epsilon\left[\frac{\sigma^{12}}{R_k^{11}r}\left(\delta^{10}+\frac{a_i}{R_k}\delta^{11}\right) - \frac{\sigma^6}{R_k^5 r}\left(\delta^4+\frac{a_i}{R_k}\delta^5\right)\right], \tag{13}$$

where z is the number of water molecules in cage k and

$$\delta^n = \frac{1}{n}\left[\left(1-\frac{r}{R_k}-\frac{a_i}{R_k}\right)^{-n} - \left(1+\frac{r}{R_k}-\frac{a_i}{R_k}\right)^{-n}\right]. \tag{14}$$

The three parameters ϵ, σ and a required for the Langmuir constants are fitted to hydrate equilibrium data. However, here we took the parameters from Kalorazi (1995) and the corresponding values are ϵ/k = 171.97, σ = 2.904 Å and a = 0.7530 Å.

2.3 The calculation method

Following the procedure given in Parrish and Prausnitz (1972), by fixing a reference state at $P_0 = 0$ bar and $T_0 = 273.15$ K, it is possible to rewrite Eq. (2), using the Gibbs-Duhem relation as

$$-\Delta\mu_w^{\beta-H} = \Delta\mu_0(P_0,T_0) - RT\int_{T_0}^{T}\frac{\Delta H_L^\beta(t)}{t^2}\mathrm{d}t + \int_{P_0}^{P}\Delta V_L^\beta \mathrm{d}p - RT\ln(a_w^L(P,T)), \tag{15}$$

where $a_w^L(P,T)$ is the activity of water in the liquid solution. Substituting Eq. (10) in the left hand side, using a standard correlation for the difference between molar enthalpies, assuming incompressibility in the liquid and empty hydrate phases and dividing both hands of Eq. (15) by RT (Sloan and Koh, 2008) we have

$$\frac{\Delta\mu_0}{RT_0} - \int_{T_0}^{T} \frac{(\Delta H_0 + \int_{T_0}^{T} \Delta C_p(t')\mathrm{d}t')}{Rt^2}\mathrm{d}t + \frac{\Delta V_0}{RT}(P - P_0) = \ln\left(a_w^L\right) - \sum_k v_k \ln\left(1 - \sum_i Y_{ik}\right) \tag{16}$$

Here, $\Delta\mu_0 = -1297$ kJ/mol, $\Delta H_0 = -4620$ kJ/mol and $\Delta V_0 = 4.6 \times 10^{-6}\ m^3$/mol (Chapoy *et al.*, 2012) is the change in chemical potential, molar enthalpy and molar volume between the β and liquid water phase at the reference point. The difference between molar specific heats is given by $\Delta Cp(T) = -37.32 + 0.179(T - T_0)$ (Chapoy *et al.*, 2012). From Eq. (16) above, we see that the function

$$F(P,T) = \frac{\Delta\mu_0}{RT_0} - \int_{T_0}^{T} \frac{(\Delta H_0 + \int_{T_0}^{T} \Delta C_p(t')\mathrm{d}t')}{Rt^2}\mathrm{d}t + \frac{\Delta V_0}{RT}(P - P_0) - \ln\left(a_w^L\right) + \sum_k v_k \ln\left(1 - \sum_i Y_{ik}\right) \tag{17}$$

has value 0 at the hydrate equilibrium curve.

The calculation procedure is as follows. First, for a given P and T, a standard Flash calculation is done by specifying the absolute amounts of water, carbon dioxide and ethanol in the liquid and vapor phases. Then, the value of the function F is calculated. This is done repeatedly, using the secant method, for different values of P, until it is found that $F(P,T) < 10^{-6}$. Then, the final value of P is the corresponding equilibrium pressure corresponding to T.

3. EXPERIMENTAL PROCEDURE

3.1 The Apparatus

Figure 1 presents the schematic diagram (Fig.1a) and a photo of the experimental apparatus (Fig. 1b). The experimental apparatus is composed by four units: CO_2 cylinder, thermostated bath (TB, JULABO F12), syringe pump (SP, Teledyne ISCO 260D) and a multiphase equilibrium module.

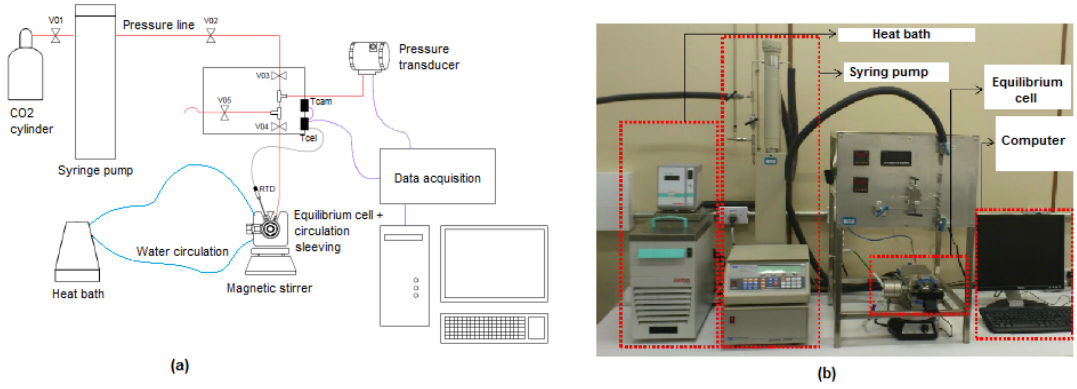

Figure 1. Experimental apparatus. (a) Schematic and (b) Photo

The equilibrium cell is made of stainless steel (AISI 316). It operates at high pressure (maximum working pressure of 25 MPa) at a range temperature from 233 up to 473 K). The cell operates at horizontal position and it has inner diameter of 17.2 mm and length of 176 mm, providing a maximum volume of 25 cm^3. The cell has two inlets: one for connecting the thermocouple and one for the injection valve. It has two sapphire windows for viewing. For the temperature control of the cell is used a cooling jacket which is coupled to the heat bath. The equilibrium cell is illuminated by a LED lamp through the lateral sapphire window in order to facilitate the visualization of phase transitions. The images are recorded by a digital camera with a resolution of 1080p.

The temperature measurement uncertainty was estimated at ± 0.17 K (95% confidence level) and the absolute preassure measurement uncertainty was $\pm 0.30\%$ of the absolute reading (95% confidence level).

3.2 Materials

Degassed and deionized water (resistivity greater than 18.2 mΩ-cm at 297 K) was used and supplied by a MILI-Q system with a filtering membrane of 0.22 μm, free of dissolved or colloidal organic and ionic contaminants. The carbon dioxide used had a minimum purity of 99.995%. Ethanol used had a purity of 99.8%.

3.3 Experimental Isothermal Procedure

Initially, the equilibrium cell was carefully cleaned and the apparatus was assembled. The procedure started with the estimation of the expected composition and parameters of the phase transition. Water and ethanol injection was carried out manually using a plunger syringe at ambient pressure and carbon dioxide was injected using a syringe pump. A digital camera was used to observe the physical state of the phases and a magnetic stirrer was used to assist the system to reach its equilibrium state faster. After the assembly of apparatus, the cooling jacket was set at a prescribed constant temperature. Next, the equilibrium cell was pressurized in order to form hydrate.

The initial pressure value was about 5 bars above the predicted equilibrium pressure for that same temperature, based on data from the NIST database (Kroenlein *et al.*, 2009). Once it was observed that the hydrate was formed, the cell was depressurized at slow and gradual steps (by increasing the volume) in order to dissociate the hydrate. These steps would be initially 1 bar, taking 20 minutes each, i.e., 0.05 bar/min. Between those steps, the volume of the pump was kept fixed for 10 minutes, in order to verify an increase of the pressure, which indicates dissociation of hydrate. If there was no increase, the same step would be repeated. When the pressure was seen to increase between steps, the volume was kept fixed until the pressure stabilizes. Then, a smaller decrease of 0.5 bar was performed in order to take again the system out of equilibrium. The rate of decrease was reduced to 0.015 bar/min. The pressure was seen to increase to the same value. This would be repeated, with gradually decreasing pressure drops, until total dissociation of the hydrate. Figure 2 below is a plot of the pressure versus time during the dissociation of carbon dioxide hydrate at 275.65 K, showing the procedure adopted.

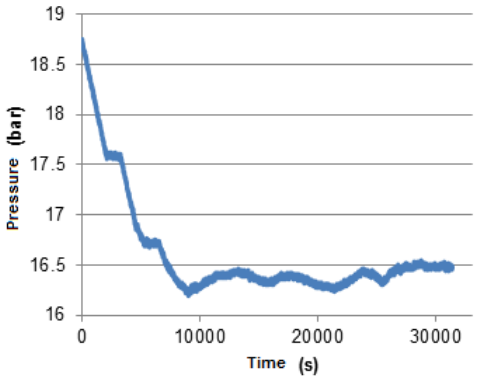

Figure 2. Plot of pressure versus time for the dissociation at $T = 275.65$ K. The equilibrium pressure was 16.5 bar.

4. RESULTS

In Figure 3, it is shown the experimental points obtained in this study. We can see the uninhibited points, with pure CO_2 and water, and the methanol (10% mass) inhibited points. Pressure increases about 30% when 10% mass of ethanol is added to this system, as we can observe ins this figure.

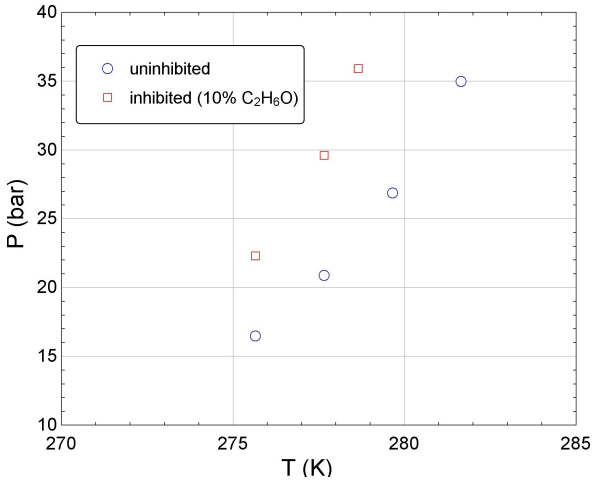

Figure 3. Experimental P versus T curves for CO_2 hydrates.

Figure 4 shows the logarithmic plot of formation pressure versus inverse absolute temperature. We can compare

the experimental points obtained in this study with literature data. We see a good agreement between the experimental equilibrium points of this work and previous studies. The straight line appearance of this plot is a consequence of the Clausius-Clapeyron equation (Smith *et al.*, 2004). Clausius-Clapeyron equation (Eq. (18)) says that semilogarithm plots of formation pressure versus reciprocal absolute temperature yeld straight lines, over limited temperature ranges, for hydrate formation (Sloan and Koh, 2008). From Eq. (18) such linear plot indicates the hydrate heat of formition,ΔH. Here, z is the compressibility factor and R is the universal gas constant. This equation enables the calculation of ΔH, which is difficult to measure experimentally.

$$\frac{dlnP}{d(1/T)} = -\frac{\Delta H}{zR} \tag{18}$$

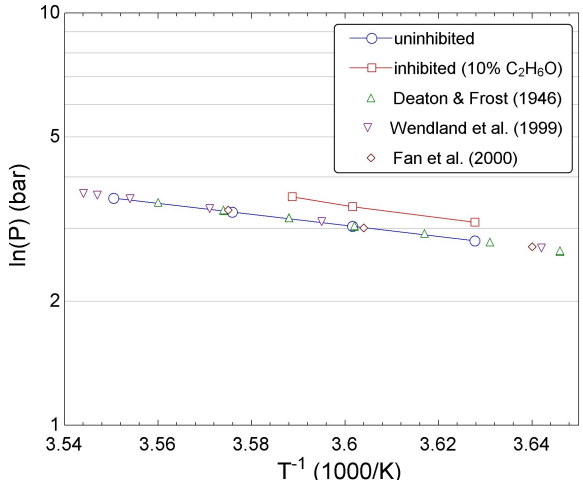

Figure 4. Logarithmic plot of formation pressure versus inverse absolute temperature.

Figure 5 shows the results for the thermodynamic model. It can be observed that the model predicted satisfactorily the formation pressure, mainly for pure CO_2. The average abolute deviation (AAD) for uninhibited CO_2 hydrate is about 6.6%. In addition, for 10% mass ethanol inhibition, the AAD is about 15%. In this study, the Kihara parameters (Eq. (14)) were taken from literatura (Kalorazi, 1995). However, if this parameters were fitted to the hydrate equilibrium formation pressure the model results, mainly for inhibited systems, would be superior.

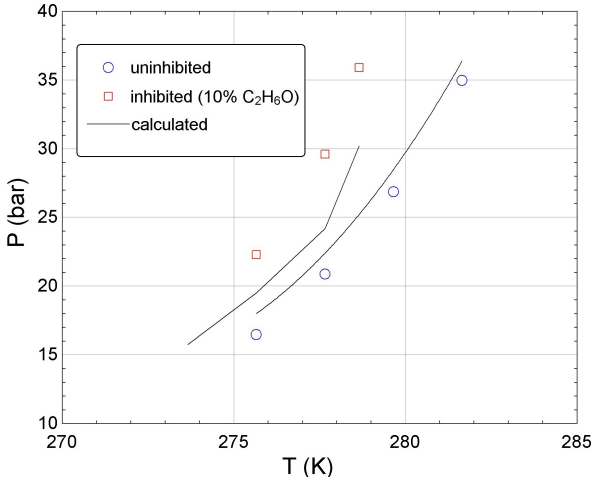

Figure 5. Thermodynamic models versus experimental points.

5. CONCLUSIONS

An experimental and modeling study was presented on the CO_2 hydrate phase equilibrium in the presence of ethanol inhibitor. An isothermal experimental procedure was presented and the experimental points were compared with literature data. A good agreement was verified, indicating that the experimental methodology adopted here is valid. Hydrate pressure equilibrium increased about 30% when 10% by weight of ethanol was added to the system.

A hydrate model (van der Waals-Platteeuw theory) togheter with the Cubic Plus Association equation os state was implemented to predict the CO_2 hydrate phase equilibrium. Satisfactory agreement was obtained between the model and experiments. The lager deviations were observed when 10% by weight of ethanol is added to the system.

6. ACKNOWLEDGEMENTS

The authors acknowledge the financial support from ANP and FINEP through the Human Resources Program to oil and gas segment PRH-ANP (PRH 10 - UTFPR) and from TE / CENPES / PETROBRAS.

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