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INHIBITION OF CARBON DIOXIDE HYDRATES BY ETHANOL AND SODIUM CHLORIDE

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Abstract. *In view of the possibilities for hydrate formation caused by carbon dioxide-rich fluids in the Brazilian Pre-Salt fields' production lines, this study focus on experimental measurements to obtain fundamental insight into the phase behavior of carbon dioxide hydrate forming systems. In this study, the carbon dioxide hydrate phase behavior was measured using a high-pressure equilibrium cell in the temperature range of 273-279 K and pressures up to 5.1 MPa. Experimental measurements were performed using a static-synthetic apparatus and isothermal method by monitoring the pressure response of the system with volume changes for hydrate dissociation. Hydrate equilibrium conditions (L_W-H-V) were obtained for CO_2 in aqueous solution of 0.02, 0.05, 0.10 and 0.15 NaCl mass fraction and 0.02, 0.05, 0.10 and 0.15 ethanol mass fraction. In addition, the inhibiting effect on the formation of hydrates at constant pressure was compared.*

Keywords: *hydrates, carbon dioxide, inhibitors, inhibiting effect.*

1. INTRODUCTION

Gas hydrates are ice-like non-stoichiometric compounds formed by hydrogen-bonded water molecules arranged in polyhedral cavities stabilized by trapped water and gas molecules such as those composing gas natural. Typical natural gas molecules include methane, ethane, propane, and carbon dioxide (Sloan and Koh, 2008).

Carbon dioxide hydrate, $CO_2 \cdot nH_2O$ ($n \geq 5.75$), crystallizes as sI, 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 at a ratio of 1:3. CO_2 hydrate is stable over a range of elevated pressure and low-temperature conditions (Adisasmito *et al.*, 1991). Carbon dioxide exhibits a higher solubility in water due to the polar attractive forces that cause the mixture to be more susceptible to hydrate formation compared to methane and other natural gas constituents (Sloan and Koh, 2008).

One of the problems with natural gas production in the pipes is gas hydrate formation which can lead to blockage (Sloan and Koh, 2008). During the transportation and processing, especially when the produced gas is water saturated and under cold conditions, gas hydrate formation may plug pipelines, valves, and other pieces of equipment. Operating outside the hydrate zone is a common practice in the oil and gas industry to prevent hydrates from forming. To expand the hydrate free-zone hydrates, thermodynamic hydrate inhibitors (e.g. alcohols, glycols and electrolytes) are used. Applying inhibitors shifts hydrate free zone to lower temperatures or higher pressures through reduction of water activity so that the gas hydrates are not formed in the flowline.

In Brazil, the pre-salt fields have been found to contain significant amounts of carbon dioxide (Melo *et al.*, 2011). This scenario emphasizes the importance of evaluating the phase equilibrium aspects inherent to carbon dioxide hydrates and their formation. In general, produced water contains various quantities of salts, naturally expanding the hydrate free zone. In cases where the inhibition effect of the produced saline water is not sufficient to prevent hydrate formation, thermodynamic inhibitors could be injected into the pipelines, resulting in a system containing both salts and inhibitor. Accurate knowledge of gas hydrate dissociation conditions in the presence of aqueous solutions of salts and/or thermodynamic hydrate inhibitors is therefore crucial to avoid gas hydrate.

This paper presents an experimental study for CO_2 hydrates inhibited with sodium chloride (0.02, 0.05, 0.10 and 0.15 mass fraction) and ethanol (0.02, 0.05, 0.10 and 0.15 mass fraction) in the three-phase equilibrium conditions of liquid water-hydrate-vapour (L_W-H-V). Experiments by the static-synthetic method and isothermal procedure at temperatures ranging from 273 to 279 K and pressures up to 5.1 MPa were conducted in an equilibrium cell. The experimental data are compared with literature data on dissociation conditions of carbon dioxide hydrates in the presence of pure water to show the inhibiting effects of the aforementioned inhibitors in aqueous solutions.

2. EXPERIMENTAL

2.1 Experimental Set-up and Chemicals

Table 1 contains the purities and suppliers of the chemicals used in this work. Aqueous solutions were prepared according to a gravimetric method, using an accurate analytical balance (mass uncertainty ± 0.0001 g). Consequently, uncertainties on the basis of mole fraction are estimated to be < 0.01. Degassed and deionized water (MILI-Q) was used in all experiments.

Table 1. Purities and suppliers of chemicals

Chemical	Supplier	Mole Fraction purity
Carbon Dioxide	White Martins	0.99995
Sodium Chloride	Biotec	0.99000
Ethanol	Vetec Chemicals	0.99800

The hydrate equilibrium conditions of the systems containing (water + carbon dioxide + sodium chloride) and (water + carbon dioxide + ethanol) have been determined using an equilibrium cell and a static-synthetic method. The schematic layout of the experimental setup is shown in Fig. 1. The equilibrium cell is a horizontal cylindrical vessel made of stainless steel with a total volume of 25 cm^3. The maximum working pressure is 25 MPa, and a temperature range from 233 to 473 K. The cell is equipped with two sapphire windows which allow phase transition observations.

A magnetic mixer (with a variable speed) was used to reduce the equilibrium time between the phases. A platinum resistance thermometer with an accuracy of ±0.17 K (95% confidence level) was used to read the temperature of the equilibrium cell. The absolute pressure measurements were made with an uncertainty of ±0.30% of the absolute reading (95% confidence level). A thermostatic bath controls the temperature cell whereas the pressure is controlled with a syringe pump. The images are recorded by a digital camera with a resolution of 1080p.

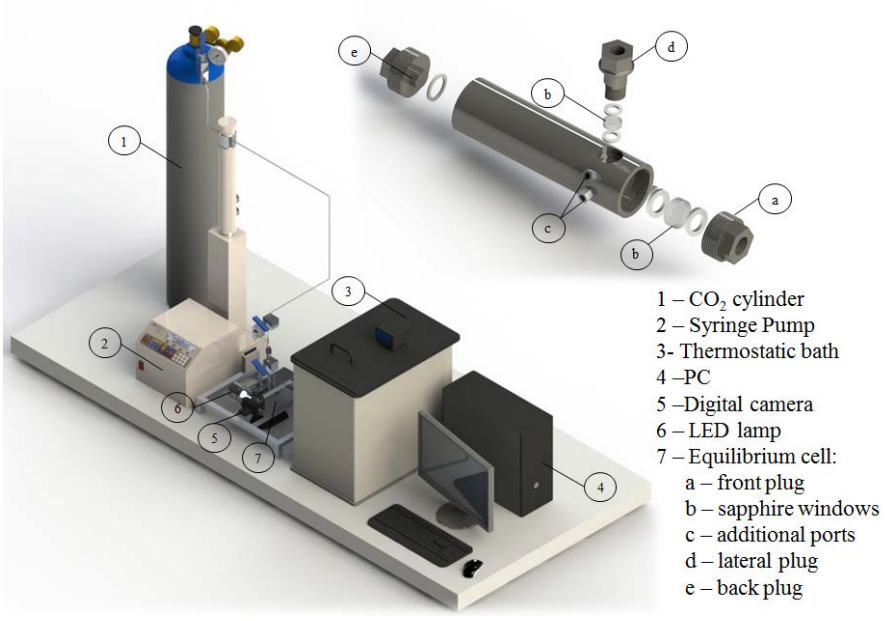

Figure 1. Schematic diagram of the experimental apparatus for hydrate equilibrium.

2.2 Experimental Procedure

The three-phase (L_W-H-V) data were measured following an isothermal procedure, as described below. Initially, the equilibrium cell is carefully cleansed and the apparatus is assembled. The cell is fed with a specified amount of aqueous solution (measured with a precision balance), for all the measurement, the amount of water is kept at 0.55 moles containing inhibitor at ambient pressure and pressurized carbon dioxide is injected using the syringe pump (Ferrari *et al.*, 2016). The temperature and pressure of the hydrate region are reached through the thermostatic bath and syringe pump, respectively. Once hydrate formation is observed, a period of about 3 hours is necessary for the system to reach equilibrium at constant temperature and pressure. After that time, the cell is slowly depressurized in gradual steps (by increasing the volume in the syringe pump) in order to dissociate the hydrate. These steps would initially be 0.1 MPa every 20 minutes, i.e., at a depressurization rate of 0.005 MPa/min. Between two steps, the volume of the pump was kept unchanged for 10 minutes, in order to verify any pressure increase that might indicate hydrate dissociation. If no pressure increase is detected, the pressure is further decreased. If the pressure increases, thus indicating hydrate dissociation, the pump volume is kept steady until the pressure stabilizes. In such case, a smaller decrease of 0.05 MPa was allowed in order to take the system out of equilibrium once again and wait for the pressure response to return the system to the same level. This process is repeated, with gradually decreasing pressure drops, until the hydrates are totally dissociated. The last pressure where hydrates are still visible corresponds to the hydrate equilibrium dissociation point. This procedure is repeated for each temperature until the hydrate equilibrium pressure is found. Fig. 2 illustrates the experimental procedure.

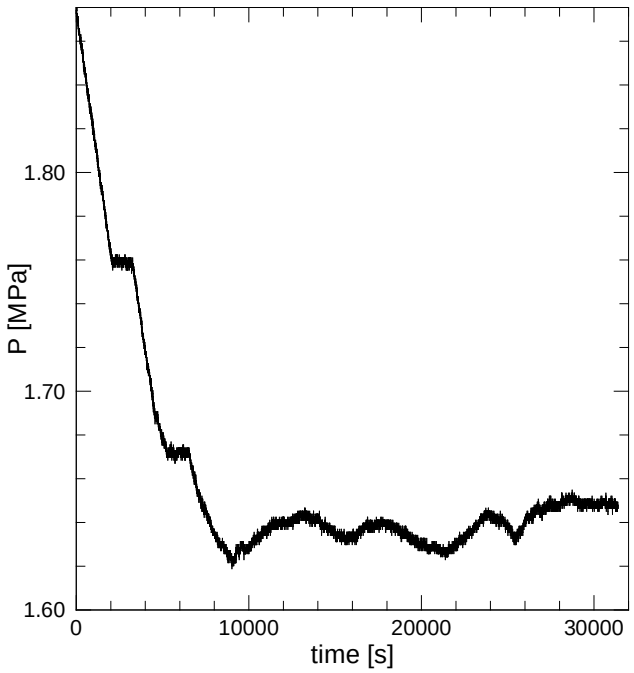

Figure 2. Pressure trace for hydrate dissociation at 275.65 K for the pure CO_2 (measured equilibrium pressure is 1.65 MPa).

3. RESULTS AND DISCUSSION

In the present study, the hydrate equilibrium conditions of (carbon dioxide + water + 0.02, 0.05, 0.10 and 0.15 mass fraction sodium chloride) and (water + carbon dioxide + 0.02, 0.05, 0.10 and 0.15 mass fraction ethanol) are measured in pressure and temperature ranges of (1.25 to 5.10) MPa and (273 to 279) K, respectively. In general, according to the Gibbs phase rule, for a ternary system consisting of gas + water + inhibitor, the three phase equilibrium has two degrees of freedom. Consequently, the pressure of the equilibrium L_W-H-V is dependent on the overall-composition of the system at a constant temperature. Sabil *et al.* (2010) showed that the L_W-H-V equilibrium data seems to be independent on the overall composition of carbon dioxide, so that the variable to be measured is the concentration of inhibitor. The L_W-H-V equilibrium curves at different concentrations of NaCl and ethanol in the system are presented in Fig. 3 and the data are tabulated in Table 2.

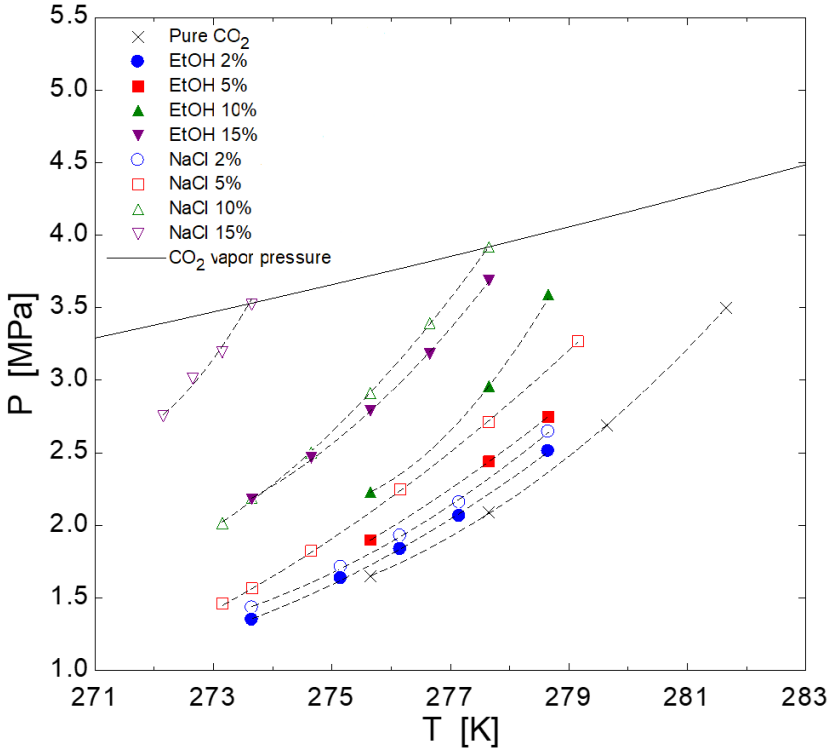

Figure 3. CO_2 hydrate equilibrium (L_W-H-V) in pure water and aqueous solutions with sodium chloride and ethanol.

Table 2. Carbon dioxide hydrate phase equilibrium conditions (L_W-H-V) in presence of inhibitors.

x_{EtOH} = 0.0434 2 mass %		**x_{EtOH} = 0.1085 5 mass %**		**x_{EtOH} = 0.2171 10 mass %**		**x_{EtOH} = 0.3256 15 mass %**	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
273.65	1.436	275,65	1.90	274,65	2.11	273.65	2.18
275.15	1.715	277,65	2.44	275,65	2.23	274.65	2.47
276.15	1.931	278,65	2.75	277,65	2.96	275.65	2.79
277.15	2.159	279,65	3.43	278,65	3.59	276.65	3.18
278.65	2.647					277.65	3.69
x_{NaCl} = 0.0342 2 mass %		**x_{NaCl} = 0.0855 5 mass %**		**x_{NaCl} = 0.171 10 mass %**		**x_{NaCl} = 0.2567 15 mass %**	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
273.65	1.259	273.15	1.463	273.15	2.016	272.15	2.751
275.15	1.517	273.65	1.539	273.65	2.187	272.65	3.011
276.15	1.746	275.15	1.825	274.65	2.501	273.15	3.194
277.15	2.061	276.15	2.247	275.65	2.912	273.65	3.579
278.65	2.593	277.15	2.712	276.65	3.395		
		279.65	3.268	277.65	3.919		

Figure 3 shows that the data sets for carbon dioxide hydrate equilibria in each solution are essentially parallel to the curve for pure water, beside that, the addition of inhibitor extends the equilibrium conditions for carbon dioxide hydrates to higher pressure at a fixed temperature. That for a given pressure, the hydrate formation temperature decreases as the inhibitor concentration increases, i.e., the addition of sodium chloride and ethanol inhibits the formation of carbon dioxide hydrate and that inhibiting effect is concentration dependent. Also shown in the figure is the carbon dioxide vapor pressure line to indicate the upper limit of the L_W-H-V equilibrium line.

To examine the hydrate inhibiting effect of electrolyte, the hydrate equilibrium data for systems with NaCl are compared with systems contain ethanol in same mass fraction. In these curves, pure CO_2 hydrate is shown to evaluate the pressure effect on equilibrium conditions. Comparing the same concentration of inhibitors, NaCl exhibited a stronger inhibiting effect than ethanol.

Sodium chloride ionizes in solution and has strong electrostatic interactions with the water molecules. The water solvating the dissolved ions are unable to form hydrates and as such, a lower temperature is needed to order the water molecules with the CO_2 molecules for hydrates to form (Sloan and Koh, 2008). As a secondary effect, the addition of NaCl in water brings about the salting-out effect, which reduces the activity of water. Therefore, the solubility of CO_2 decreases with increasing NaCl concentration, as experimentally observed by Sun *et al.* (2016). As the salt concentration is increased, more water molecules are tied up by the salt ions, decreasing the number of water molecules available to form the hydrogen bonds that cause clustering around the CO_2 molecules. Both ion clustering and salting-out act together, thus requiring substantially more subcooling to induce the structural changes and to trigger hydrate formation.

The action of ethanol as hydrate inhibitor is different from that of the sodium chloride. The hydrogen bonding of the hydroxyl group in ethanol with water molecules is the only molecular interaction that ties up water molecules making them unavailable to form hydrates. Additionally, the hydrocarbon segment of ethanol causes a clustering effect on water molecules similar to that caused by CO_2 (Sloan and Koh, 2008). As for the hydrate cluster formation, both effects compete with the solubilized CO_2 molecules. However, the hydrogen bonding of the hydroxyl group is more pronounced. In both sodium chloride and ethanol, the water activity is altered in the arrangement for the formation of the hydrate and stronger driving forces are therefore required to induce the formation (Sloan and Koh, 2008).

To evaluate the inhibition strength of sodium chloride and ethanol on the formation of hydrates, the experimental data of hydrate equilibrium were analyzed in the presence of different inhibitors concentrations at constant pressures. Fig. (4) shows that the CO_2 hydrate dissociation temperature decreases with increasing inhibitor concentration.

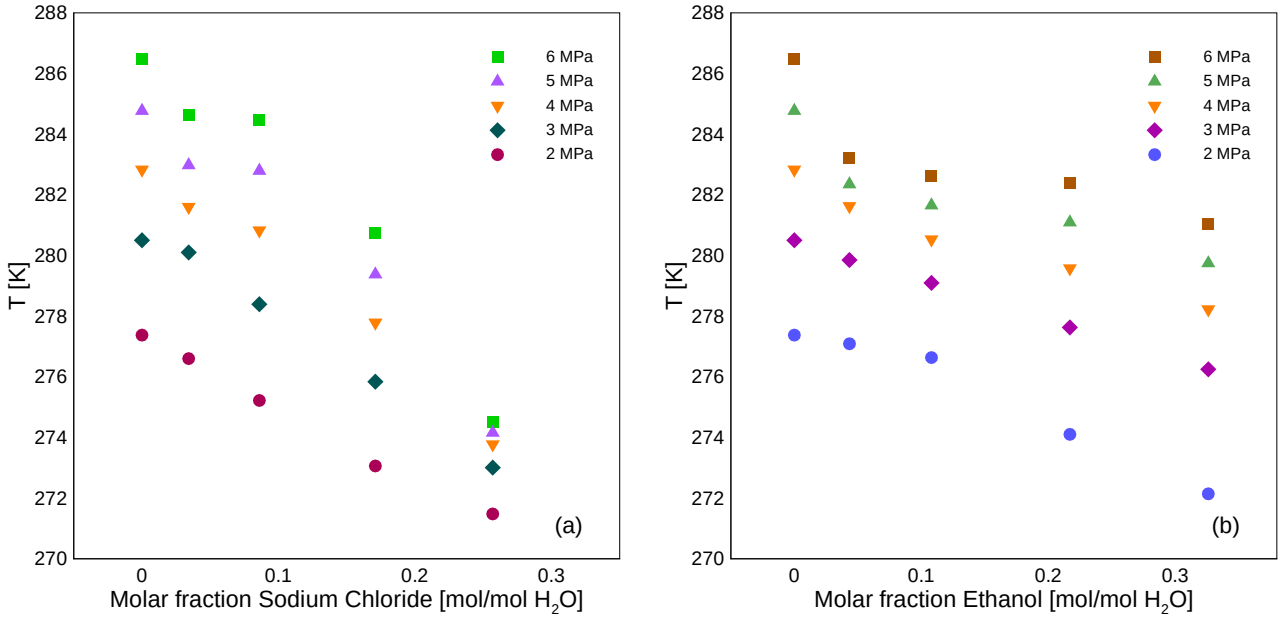

Figure 4. CO_2 hydrate equilibrium conditions at constant pressure for aqueous (a) sodium chloride and (b) ethanol solutions.

To quantify the inhibiting effects of those two inhibitors on carbon dioxide hydrate equilibria, the hydrate depression temperature, $\Delta T_H = T_0 - T_I$, between carbon dioxide hydrate equilibria in pure water (T_0) and that in the aqueous inhibitor solution (T_I) was calculated. The hydrate depression temperature was calculated assuming regression curves at fixed pressures for each set of inhibitor and concentration. Table 3 shows the hydrate depression temperature (ΔT_H) for each concentration at five different pressures, and these values are compared to the freezing point depression (ΔT) values of aqueous sodium chloride and ethanol solutions (Lide, 2003-2004).

Table 3. Hydrate Depression Temperature (ΔT_H) and Freezing Point Depression (ΔT).

System	Inhibitor molar fraction	ΔT [K]	ΔT_H [K]				
		P = 0.1 MPa	P = 2 MPa	P = 3 MPa	P = 4 MPa	P = 5 MPa	P = 6 MPa
CO_2 + H_2O + NaCl	0.034	1.190	0.770	0.970	1.030	1.790	1.830
	0.086	3.050	2.150	2.108	2.007	1.974	2.006

	0.171	6.560	4.310	4.661	5.044	5.393	5.715
	0.257	10.915	5.891	7.495	9.058	10.613	11.969
CO_2 + H_2O + EtOH	0.043	0.810	0.470	0.650	1.205	2.420	3.270
	0.108	2.090	0.735	1.405	2.301	3.115	3.857
	0.217	4.470	3.267	2.872	3.255	3.678	4.090
	0.326	7.370	5.229	4.253	4.607	5.025	5.439

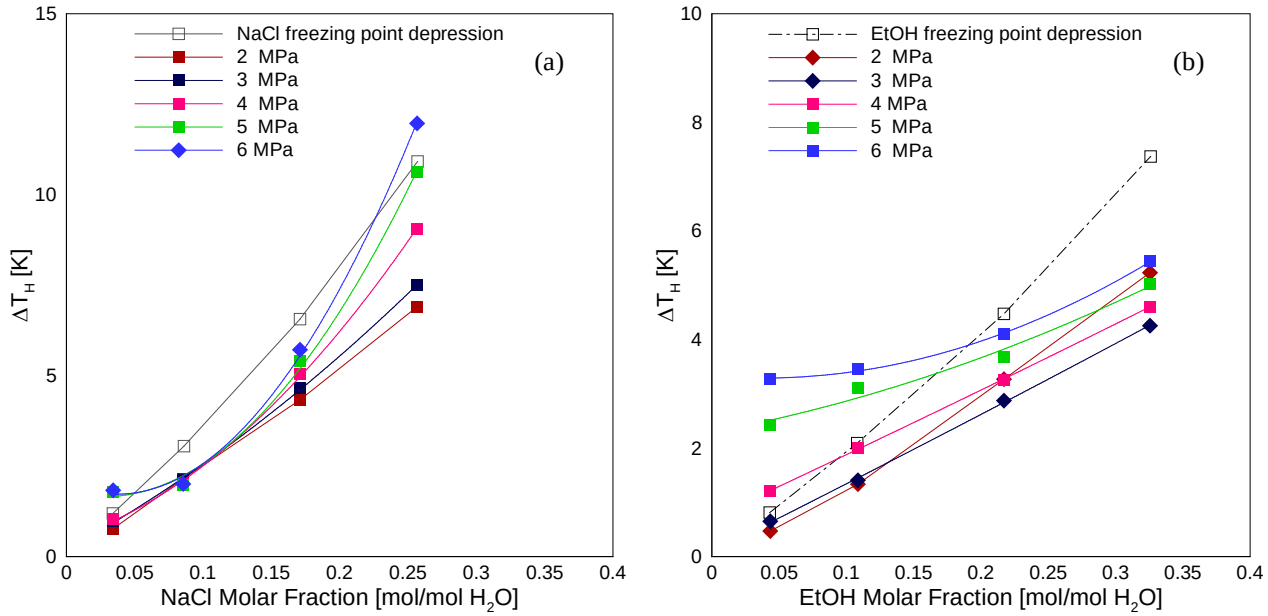

Figure 6. Hydrate depression temperature for (a) sodium chloride and (b) ethanol.

In Fig. 6, it can be observed that, as the pressure increases, increasing NaCl concentrations in aqueous solutions result in higher depression temperature. This can be understood by the decrease in the CO_2 solubility in the inhibited aqueous phase as the salt concentration increases (salting-out effect). The Coulombic forces and the salting-out effect seem to make NaCl a better inhibitor than ethanol.

It is also observed in Fig. 6 that a reversing trend in the hydrate depression temperature at higher pressures for lower inhibitor concentration, which shows that ethanol has a higher inhibition effect than sodium chloride. This can be attributed to the selective solubility caused by the pressure effect and such behavior can be attributed to the salting-in effect for NaCl, that is, the solubility of CO_2 increases at low salt concentrations. The salting-in effect at low concentrations is explained by the Debye-Huckel theory (Debye and Huckel, 1923).

4. CONCLUSIONS

The equilibrium conditions for carbon dioxide hydrates formed in the presence of aqueous solutions of sodium chloride and ethanol were experimentally measured at temperatures ranging from 272.15 to 279.65 K and pressures up to 3.91 MPa using the isothermal method. The experimental three-phase equilibrium data (L_W-H-V) were compared with those in the literature, showing consistent agreement.

The hydrate depression temperature was used to compare the inhibiting effect of the sodium chloride and ethanol in the carbon dioxide hydrate equilibrium. Two trends were observed. For higher inhibitor concentrations, with increasing pressure, higher depression temperature were observed for sodium chloride, indicating that it is a stronger hydrate inhibitor than ethanol at the same mole fraction. Yet, for lower inhibitor concentrations, ethanol exhibited a higher inhibition effect than sodium chloride. Those two trends can be attributed to the selective solubility caused by the pressure effect and the salting-out and salting-in effect for the CO_2 solubility.

5. ACKNOWLEDGEMENTS

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