PHASE BEHAVIOR OF CARBON DIOXIDE HYDRATE SYSTEMS: A COMPARISON BETWEEN SODIUM CHLORIDE AND ETHANOL INHIBITION EFFECTS

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Abstract. *In view of the possibilities for hydrate formation caused by carbon dioxide-rich fluids in the Pre-Salt fields' production lines, this study focus on experimental measurements that were carried out so as to obtain fundamental insight into the phase behavior of carbon dioxide hydrate forming systems. This work focus on the influence of sodium chloride, a hydrate inhibitor, on the phase behavior and its implications in practical applications. In addition, the inhibition effect of the ethanol on hydrates is compared with that of sodium chloride at the same mass fraction. The phase behavior of carbon dioxide hydrate in the presence of ethanol was obtained in a previous experimental study. In the present study, the carbon dioxide hydrate phase behavior was measured using a high pressure equilibrium cell in the temperature range of 273-279 K. Experimental measurements were performed using the isothermal method by monitoring the pressure response of the system with volume changes. By taking advantage of the availability of the measured three-phase (L_W-H-V) data, the enthalpy of dissociation of simple carbon dioxide and inhibited hydrates is estimated by using the Clausius-Clapeyron equation. Results showed that at the same mass fraction of inhibitor, sodium chloride exhibited a superior inhibition effect compared to that of the ethanol.*

Keywords*: hydrates, ethanol, sodium chloride, inhibition effect.*

1. INTRODUCTION

Carbon dioxide hydrate, $CO_2 \cdot nH_2O$ ($n \geq 5.75$), belongs to the family of gas hydrates: nonstoichiometric, ice-like crystalline compounds formed by hydrogen-bonded water molecules arranged in polyhedral cavities stabilized by trapped gas molecules. CO_2 hydrate crystallizes in one of the three 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 at a ratio of 1:3. CO_2 hydrate is stable over a range of elevated pressure and low-temperature conditions (Sloan and Koh, 2008). Gas hydrates are easily formed during the transportation of oil and gas when it contains a certain amount of water, resulting in pipeline blockages and other operational problems in the petroleum industry. During the transportation and processing, especially when the produced gases contain saturated water steam and under cold environmental conditions, gas hydrate may plug pipelines, valves, and other pieces of equipment.

Operating outside the hydrate zone is the common practice in the oil and gas industry to prevent hydrate formation. There are several methods to either prevent, halt or even to revert hydrate formation in situations where they are likely to form. In some cases, simple manipulation of the system temperature and pressure may suffice to avoid hydrates. Water removal or dehydration can be very effective. However, in some cases the implementation of one of these methods may not be cost effective. In those situations, the injection of thermodynamic inhibitors, such as alcohols and salts, is often an option due to their inherent properties of hydrate suppression. The knowledge of gas hydrate phase equilibrium in the presence of alcohol or salt aqueous solutions is therefore essential to estimating the boundaries of the gas hydrate formation zone.

In the early 1820s, John Faraday investigated the newly discovered gas, chlorine. He was reproducing the formation of solid chlorine "ice", as observed by Humphrey Davy in 1810 (Sloan and Koh, 2008). Faraday then verified that water was the host molecule with chlorine molecules as the guest. These experiments were the first reference to a class of associative compounds presently known as gas hydrates (Faraday and Davy, 1823). A century later, Hammerschmidt demonstrated that the "ice" was actually gas hydrates (Hammerschmidt, 1934) and then Deaton and Frost (Deaton and Frost, 1946) experimentally investigated the formation of hydrates from pure components of natural gases.

Despite the existence of some publications devoted to experimental investigation of CO_2 hydrate phase equilibrium in sodium chloride aqueous solutions (Larson, 1955; Vlahakis, 1972; Englezos *et al.*, 1988; Adisasmito *et al.*, 1992; Diamond, 1992; Dholabhai *et al.*, 1993; Sabil *et al.*, 2009; Lee *et al.*, 2011) and ethanol aqueous solutions (Mohammadi, 2005; Maekawa, 2010; Makiya et al., 2010) there is a lack of studies dealing specifically with the comparison between both inhibitors.

This paper is a sequence of a previous study (Ferrari *et al.*, 2016) in which the dissociation conditions of CO_2 hydrates in the presence of ethanol aqueous solutions was reported. In this work, further data on CO_2 hydrates inhibited with sodium chloride are reported in the three-phase equilibrium conditions of liquid water-hydrate-vapour (L_W-H-V). In addition, the experimental data are compared with literature data on dissociation conditions of carbon dioxide hydrates in the presence of pure water to show the inhibition effects of the aforementioned inhibitors in aqueous solutions. 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.

2. EXPERIMENTAL

2.1 Materials and Apparatus

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

An equilibrium cell to study the condition in which hydrates dissociate was used. The schematic layout of the experimental setup is shown in Fig. 1. The 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. The cell's temperature and pressure can be measured with a Pt-100 RTD and pressure transducer (Wika s-11), respectively. 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.

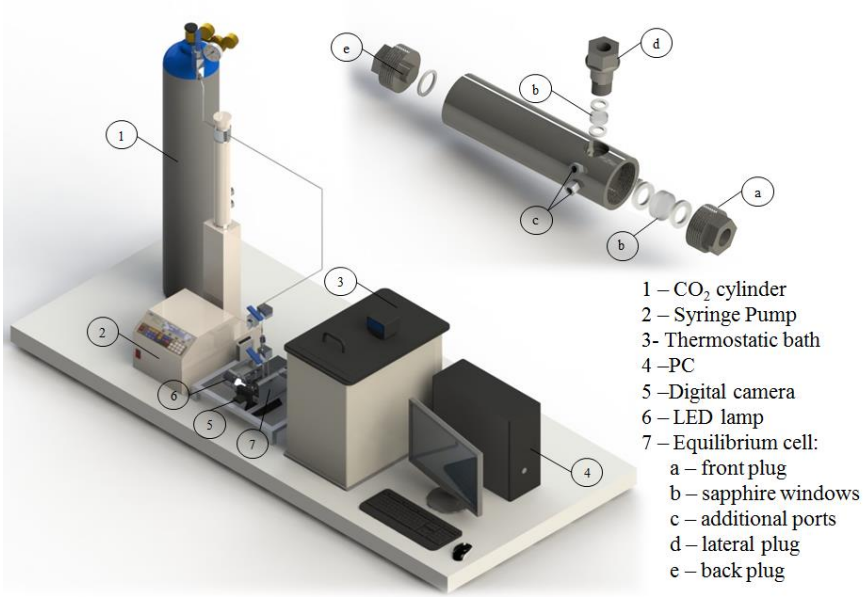

Figure 1. Schematic diagram of the experimental apparatus for hydrate equilibrium.

2.2 Procedure

The three-phase (L_W-H-V) data were measured with an isothermal procedure, as described below. The cell is fed with the aqueous solution containing inhibitor (50% of the cell volume was filled with the aqueous solution) at ambient pressure and pressurized carbon dioxide was injected using the syringe pump.

The temperature and pressure of the hydrate region are achieved through the thermostatic bath and 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, the cell is depressurized at slow and gradual steps (by increasing the volume in the syringe pump) in order to dissociate the hydrate. These steps would initially be 0.1 MPa, taking 20 minutes each, i.e., at a depressurization rate of 0.005 MPa/min. Between two steps, the volume of the pump was kept fixed for 10 minutes, in order to verify any pressure increase, which would indicate hydrate dissociation. Then, a smaller decrease of 0.05 MPa was allowed in order to take the system out of equilibrium once again. The depressurization rate was reduced to 0.0015 MPa/min. It was observed that the pressure increased and reached the same value. This would be repeated, with gradually decreasing pressure drops, until total dissociation of the hydrate. This procedure was repeated for each temperature. See Ferrari *et al*. (2016) for more details about the experimental procedure.

The uncertainties for the hydrate dissociation temperatures and pressures are estimated at ±0.17 K (95% confidence interval) and ±0.30% of the absolute reading (95% confidence interval), respectively.

3. RESULTS AND DISCUSSION

Hydrate dissociation conditions (*T* and *P*) for the (CO_2 + H_2O) systems were measured for different compositions of the aqueous solution containing NaCl. The NaCl mass concentrations of the aqueous solutions together with their dissociation conditions are presented in Tab. 2. Figure 2 shows the semi-logarithm plot of the dissociation pressure versus the inverse of the absolute temperature measured in this work along with some selected experimental data from the literature on NaCl aqueous solution (Dholabhai *et al.* (1993); Adisasmito *et al.* (1992); Tohidi *et al.* (1997) Sabil *et al.* (2009)). As it can be seen, the agreement between these data and the experimental data reported in the literature is generally acceptable, demonstrating the reliability of the apparatus and method used in this work. The linear behavior of this plot comes as a consequence of the Clausius-Clapeyron equation (Smith et al., 2001; Sloan and Koh, 2008).

$$\frac{d\ln P}{d\left(1/T\right)} = -\frac{\Delta H}{ZR} \tag{1}$$

In Eq. (1), *Z* is the compressibility factor and *R* is the universal constant of the gases. The linear plot indicates the hydrate heat of formation, ΔH, which is difficult to measure experimentally.

Table 2. Dissociation points of CO_2 Hydrates inhibited with NaCl.

Solution	T (K) ±0.17	P (MPa) ±0.3
2 wt% NaCl	273.65	1.259
	275.15	1.517
	276.15	1.746
	277.15	2.061
	278.65	2.593
5 wt% NaCl	273.15	1.463
	273.65	1.539
	275.15	1.825
	276.15	2.247
	277.15	2.712
	279.65	3.268
10 wt% NaCl	273.15	2.016
	273.65	2.187
	274.65	2.501
	275.65	2.912
	276.65	3.395
	277.65	3.919
15 wt% NaCl	272.15	2.751
	273.15	3.194
	273.65	3.579
	274.15	5.113

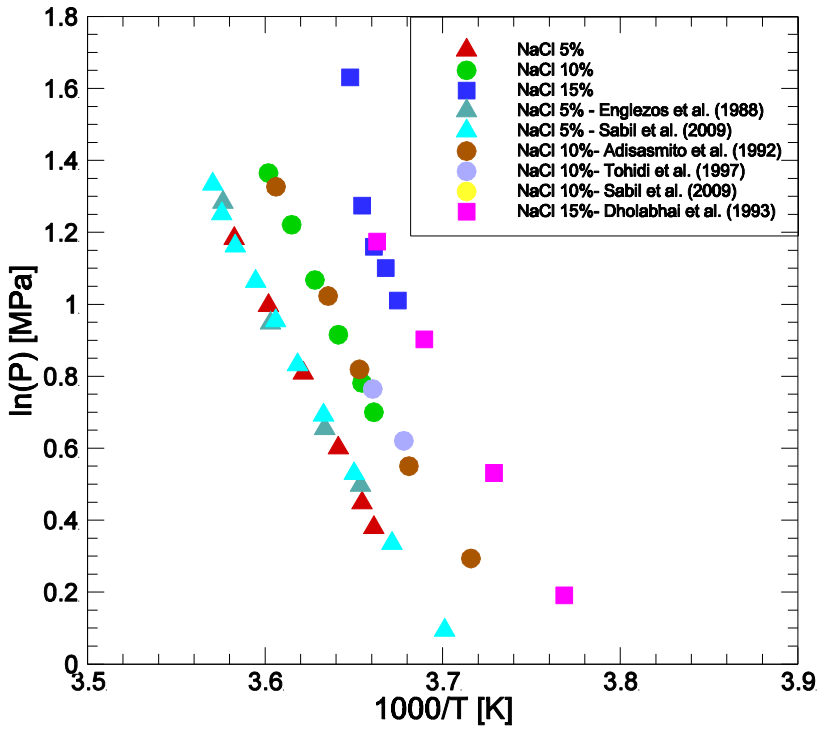

Figure 2. Logarithmic plot of dissociation pressure versus inverse absolute temperature.

Figure 3 shows all the data measured in this study for the carbon dioxide hydrate system, including those with and without ethanol (Ferrari *et al.*, 2016). Higher concentrations were not tested because the ranges of temperature and pressure were limited by two factors. First, the limit of solubility of sodium chloride in water (≈23%) could not be reached and, secondly, at higher pressures a precipitation of a new CO_2-rich liquid phase was observed.

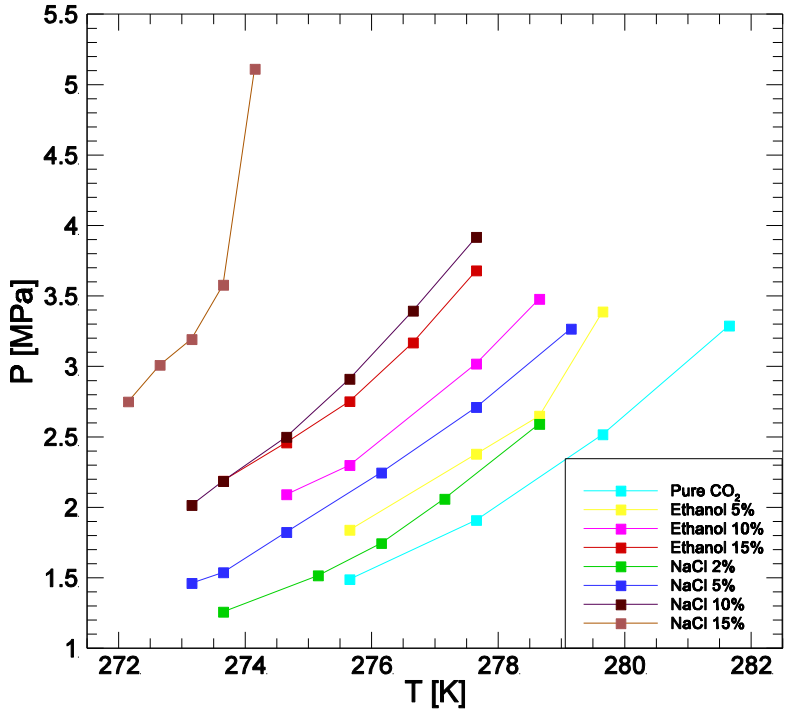

Figure 3. CO_2 hydrate equilibrium conditions in pure water and aqueous sodium chloride and ethanol solutions.

It can be seen in the Fig. 3 that the data sets for carbon dioxide hydrate equilibria in each solution are essentially parallel to the curve for pure water. For a same pressure, the hydrate formation temperature decreases as the inhibitor concentration increases.

It is known that hydroxyl groups in alcohols allow the formation of hydrogen bonds with water molecules and the hydrocarbon chain tends to arrange the water into solvent clusters. These effects increase the solubility of carbon dioxide in water and require greater driving forces to let the hydrate formation to occur. The salts ionize in aqueous solutions and those ions interact with water molecules via dipole (Coulomb) bonds. The interaction causes the water molecules to cluster around the ions, thus minimizing the water availability for the arrangement in cavities during the hydrate formation process (Sloan and Koh, 2008).

The hydrate inhibition strength is a measure for the temperature depression caused by a particular inhibitor for hydrate formation to take place. This means that the stronger the hydrate inhibition effect, the lower the hydrate equilibrium temperature will be. An inspection of the Fig. 3 shows that the comparison between the inhibition effects of ethanol and sodium chloride is not clear.

To investigate the inhibition effects of these two inhibitors on carbon dioxide hydrate equilibria, the hydrate point drop, ΔT_H, between carbon dioxide hydrate equilibria in pure water and that in an aqueous inhibitor solution was obtained, assuming that each set of carbon dioxide hydrate equilibria ran parallel to a regression curve obtained for pure water. The temperature difference was calculated using the following Eq. (2):

$$\Delta T_H = T_0 - T_I \tag{2}$$

where T_0 is the hydrate equilibrium temperature for pure water and T_I is a hydrate equilibrium temperature in the presence of inhibitor at a fixed pressure. Table 3 shows the hydrate point drop for each studied concentration at five different pressures, and these values are compared to the freezing point drop values of aqueous sodium chloride and ethanol solutions (CRC Handbook, 2004).

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

System	Inhibitor mass 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	0.02	1.190	0.379	0.91	1.278	1.574	1.831
	0.05	3.050	2.150	2.108	2.007	1.974	2.006
	0.10	6.560	4.310	4.661	5.044	5.393	5.715
	0.15	10.915	5.891	7.495	9.058	10.613	11.969
$CO_2 + H_2O$ + EtOH	0.05	2.090	0.735	1.405	2.301	3.115	3.857
	0.10	4.470	3.267	2.872	3.255	3.678	4.090
	0.15	7.370	5.229	4.253	4.607	5.025	5.439

Since there are no data for hydrate point drop values at atmospheric pressure, a strictly direct comparison could not be made. The effect of adding more inhibitor is nonlinear as is the effect on the freezing point drop.

Figure 4 compares the inhibitive effects of the sodium chloride and ethanol at specific pressures. In general, at higher concentrations, the difference between ethanol and sodium chloride is most evident. Higher salt concentrations in aqueous solutions reduce the solubility of carbon dioxide in water containing electrolytes and reduce the available free water, forcing a greater driving force for the hydrates formation to occur.

For inhibitor concentrations up to 5%, a more thorough assessment about the inhibition effect should be made. It can be observed that for pressures up to 3 MPa, sodium chloride is a better inhibitor than ethanol, suppressing the temperature by approximately 0.7 K above the temperature of the ethanol inhibition. However, ethanol shows a stronger inhibition effect for pressures above 4 MPa, with temperature drops about 1.85 K above the temperature of inhibition provided by sodium chloride.

This evaluation allows one to infer that the difference between the inhibition effect of ethanol and sodium chloride at low concentration depends upon the operating pressure. At low concentration and higher pressures, ethanol showed a stronger inhibition effect when compared to sodium chloride.

4. CONCLUSIONS

The equilibrium conditions for carbon dioxide hydrates formed in the presence of aqueous solutions of sodium chloride were experimentally measured at temperatures ranging from 272.15 to 279.15 K and pressures up to 5.11 MPa using the isothermal method. The experimental data were compared with some open literature data, and the admissible concordances between the data suggested that the experimental technique used in this study was reliable. The temperature of hydrate formation decreases with increasing inhibitor concentration, for the same pressure. The inhibition effect of chemicals on

carbon dioxide hydrate equilibrium was evaluated. At low inhibitor mass fraction (about 5%), ethanol exhibited a stronger inhibition effect at higher pressures. However, at inhibitor mass fractions higher than 5%, sodium chloride showed the best inhibition effect at any pressure.

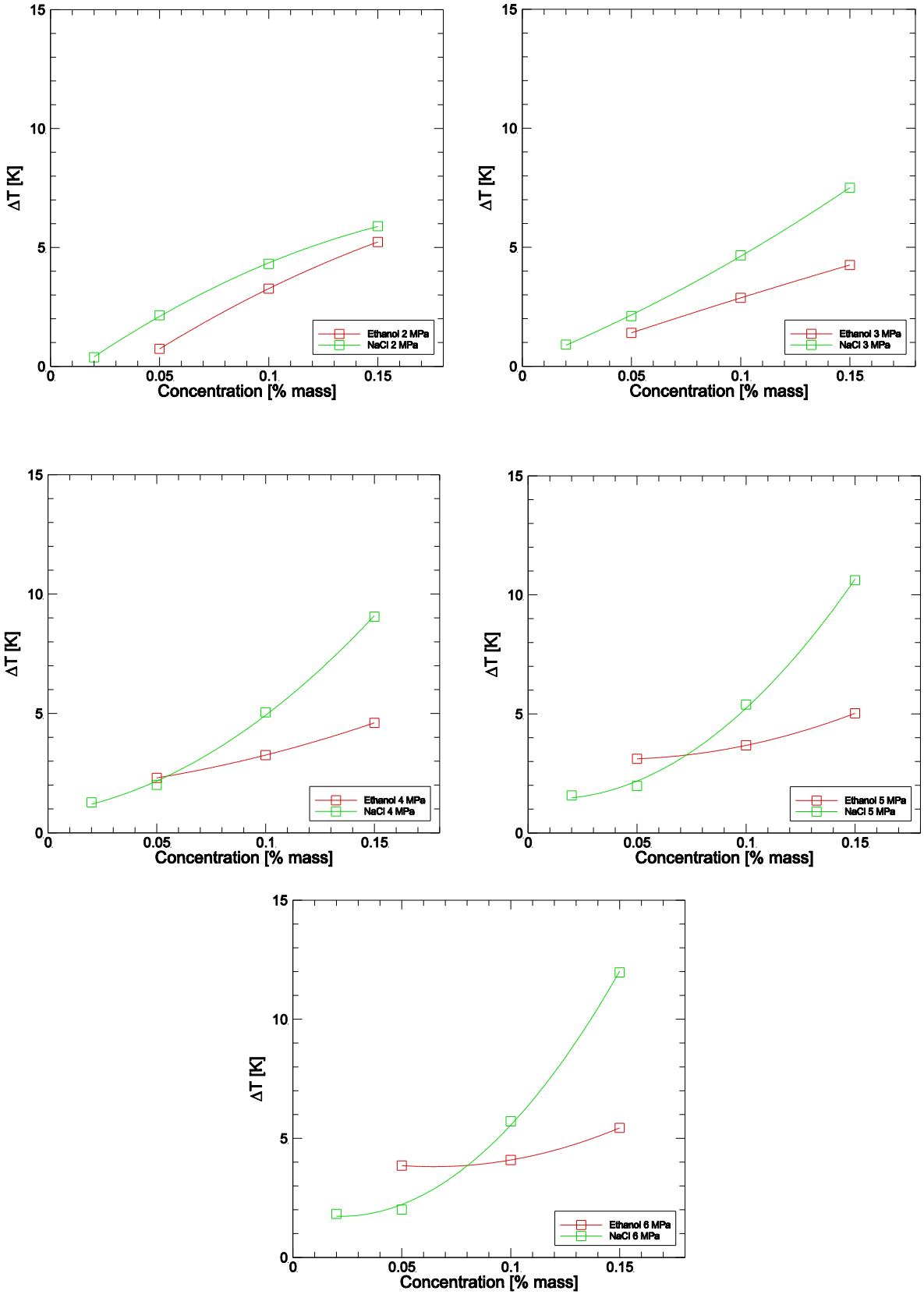

Figure 4. Hydrate point drop for sodium chloride and ethanol.

4. ACKNOWLEDGEMENTS

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