Incipient Equilibrium Data for Propane Hydrate Formation in Aqueous Solutions of NaCl, KCl, and $CaCl_2$

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Incipient equilibrium experimental data for propane hydrate formation in pure water and aqueous single, binary, and ternary solutions of NaCl, KCl, and $CaCl_2$ were obtained. Forty experiments were performed in the temperature range of 261.9–278.3 K using a new apparatus which was constructed in our laboratory. The apparatus was found to provide measurements which are reproducible and consistent with values reported in the literature. The results were compared with the predictions from a hydrate equilibrium calculation method. The agreement between the data and the predictions was found to be good.

Introduction

Gas hydrates are nonstoichiometric crystalline compounds. They are formed by water molecules which are linked together with hydrogen bonds and form a three-dimensional structure (lattice) with cavities. The cavities can be occupied by certain molecules of gases and volatile liquids. One cavity can accommodate only one molecule. These molecules should not interfere with the hydrogen bonds among the water molecules, and they should have molecular diameters which are smaller than the diameter of the cavity. The structure is by itself thermodynamically unstable (empty hydrate lattice). However, inclusion of molecules with the characteristics described above at suitable pressure and temperature conditions creates the stable hydrate crystal lattice. The most recent comprehensive description of the properties, technological significance, and implications of gas hydrates has been presented by Sloan (*1*).

Gas hydrate phase equilibrium data and predictive methods are needed for the rational design of the facilities that deal with hydrates. Electrolytes are able to suppress the formation conditions of gas hydrates. The corrosive action of the aqueous electrolyte solutions, however, prevented their wide use as inhibiting agents. In spite of their corrosive potential, electrolytes are among the constituents of drilling muds. Other reasons for obtaining the experimental data and developing predictive methods for hydrate equilibria in the presence of electrolytes are possible development of water desalination and underground gas storage facilities and occurrence of natural gas hydrate reservoirs.

Knox et al. (*2*) and Kubota et al. (*3*) studied propane hydrate formation in the presence of NaCl in order to develop a seawater desalination process via gas hydrate formation. Sloan (*1*) has the complete collection of experimental hydrate formation data, including those on the inhibiting effect of electrolytes. It should be noted that all these studies were concerned with single electrolyte solutions. Englezos and Bishnoi (*4*) and Dholabhai et al. (*5*) were the first to report equilibrium data for ethane and methane hydrate formation in the presence of mixed electrolytes. These data were found to be in very good agreement with the predicted values from a method that was presented earlier (*6*).

The objective of the present work is to report incipient equilibrium data for propane hydrate formation in the presence of single and mixed electrolytes and compare the results with the above method. The data were collected in a new apparatus that is also presented. It is shown that the experimental hydrate formation data and the predicted values agree very well.

Experimental Setup

Apparatus. A schematic diagram of the experimental apparatus is displayed in Figure 1. The vital part of the apparatus is the equilibrium cell. The cell is immersed into a temperature controlled bath. The temperature bath holds 118 L of a liquid mixture of (50:50, mass %) water and ethylene glycol to keep a constant temperature within the system. The temperature of the glycol mixture is controlled by an external refrigerator/heater; it uses a heating/cooling coil to transfer heat in and out of the temperature bath. The apparatus uses a Forma Scientific refrigerator (model 2095) with a capacity of 28.5 L. The refrigerator utilizes another solution of (50:50, mass %) of ethylene glycol and water as a heater/coolant; this solution is circulated in an enclosed loop, and heat is exchanged through the heating/cooling coil. Copper tubing was used in the construction of the coil. A motor-driven stirring mechanism is used to maintain a uniform temperature in the glycol–water mixture. A relatively constant temperature (±0.10 K) can be achieved over a long period of time using this apparatus.

Equilibrium Cell. The cell was machined from a solid 316 stainless steel cylindrical bar. A cross sectional view of the cell is illustrated in Figure 2. Two viewing windows are fitted onto the front and back, while a third window is mounted at the top of the cell. The windows were machined from $^1/_2$-in.-thick Plexiglas plates. All three windows are circular, they are held in place by stainless steel bolted studs, and they are sealed with neoprene O-rings. Six bolts were used for the windows on the sides and eight for the window on the top of the cell. The cell was tested to a pressure of 1.0 MPa.

By using a magnetic stir bar coupled with a set of magnets outside the equilibrium cell, good stirring was accomplished. The set of magnets is mounted on an aluminum housing connected to a dc motor. As the set of magnets spins around, the magnetic force couples the stir bar, causing it to spin and, hence, mixing the contents in the cell.

The temperature inside the cell is measured with two Omega copper–constantan thermocouples. One thermocouple is situated at the top half of the chamber for the gas phase, while another thermocouple is positioned near the bottom of

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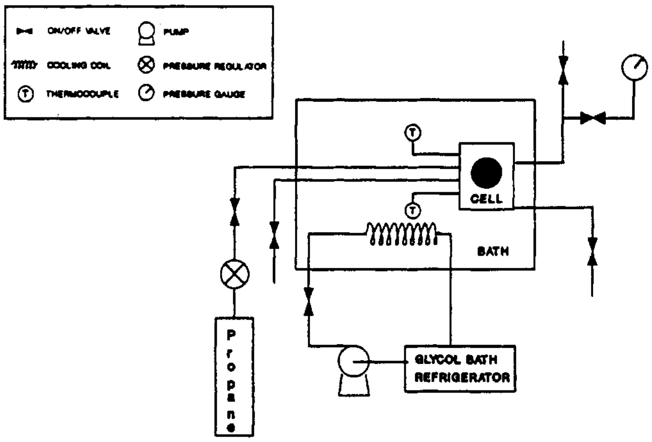

Figure 1. Schematic of the experimental apparatus.

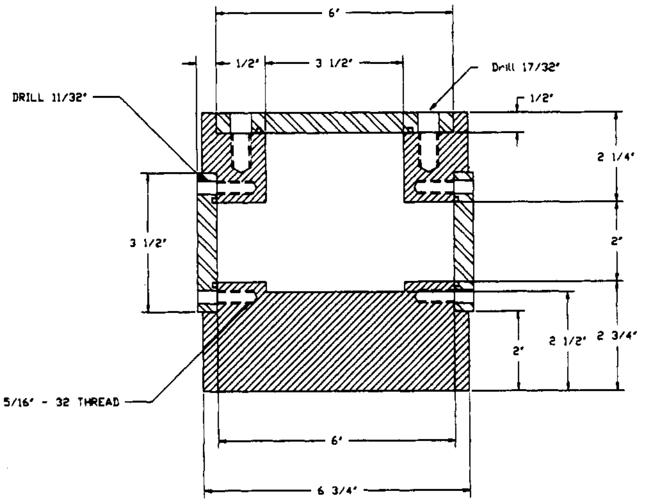

Figure 2. A cross section of the equilibrium cell.

the chamber for the liquid phase. The thermocouples were calibrated with a calibrated thermometer from Fisher Scientific and a calibrated thermistor from Paso Scientific. Their respective accuracies were ±0.03 and ±0.04 K. The accuracy of the thermocouple measurements is believed to be ±0.10 K. The pressure is measured by a 0–300 psi Bourdon tube Heisse pressure gauge from Brian Engineering. The gauge was calibrated against an Ametek Modcal pressure module (pneumatic), traceable to NIST with an accuracy of 0.05%. The accuracy of the pressure measurements is ±0.25% of the span.

Experimental Procedure

The electrolyte solutions were prepared with deionized water and laboratory grade electrolytes from Fisher Scientific. The appropriate amount of electrolytes was weighed using a Mettler balance. The readability of the balance was 0.1 mg. The electrolytes were then dissolved in deionized water. The solution was weighed with a second Mettler balance. The readability of the second balance was 0.01 g. A sample of each aqueous solution was taken in a flask and immersed into the bath in order to verify the absence of any salt precipitation at the lowest experimental temperature. Approximately 100 cm^3 of the liquid solution was injected into the cell. At each single or mixed electrolyte solution concentration that was chosen to obtain hydrate formation data, one solution was used for the measurement of the incipient equilibrium hydrate formation pressure at the various selected temperatures. After the injection of the solution into the cell, it was allowed to reach the desired constant temperature.

Propane gas from Medigas with a purity of 99.5% (by volume) is supplied to the cell and discharged in two consecutive trials for the purpose of flushing the system. For each solution, it is desired to eliminate the hysteresis phenomenon and enhance the structure in the aqueous phase. For this purpose, hydrate crystals are formed by pressurizing the cell with propane gas until the pressure is sufficient to induce nucleation of hydrates quickly. Usually, this pressure is 0.15 MPa above the calculated equilibrium hydrate formation pressure. Subsequently, the hydrate crystals are decomposed by venting the gas out of the system. Formation and decomposition of the hydrates is repeated one or two more times. These nucleation experiments are carried out only once for each solution under study.

Following the nucleation experiments, the first incipient hydrate formation pressure at a selected temperature can be measured. Incipient equilibrium conditions refer to the situation where an infinitesimal amount of hydrates is in equilibrium with the aqueous liquid phase and with the hydrocarbon-rich vapor phase. Practically, this is the situation when a small number of very tiny crystals coexist in equilibrium with the fluid phases. For this purpose, the cell is pressurized to a pressure slightly above the estimated equilibrium value. It is noted that if an approximate value of the equilibrium hydrate formation pressure at a given temperature is unknown, then an experimental trial and error procedure is performed to obtain such an estimate. It is assumed that such an estimate is known. In this case, the experiment continues by commencing the stirring of the solution contents and allowing the temperature to reach a stable value. Once the temperature is constant, the pressure is further increased to induce hydrate nucleation. This is accomplished by introducing more propane gas into the cell. The pressure is now well above the hydrate equilibrium pressure corresponding to the experimental temperature. Hence, there is a large driving force to cause hydrate nucleation. Indeed hydrates are easily formed, and once a small amount is present the pressure is quickly decreased to the estimated equilibrium value by venting some of the gas out of the system.

The system is left at these conditions for at least 4 h. If there is a small amount of hydrates in the equilibrium cell at the end of the 4-h period, and the temperature and pressure are constant, then this pressure is taken as the equilibrium pressure at this operating temperature. If no hydrates are present after the 4-h period, the system is below the equilibrium pressure. In this case, the experiment is repeated but the new estimated equilibrium pressure is set at a higher value. The experiment is terminated once the pressure and temperature are stable and a small number of very tiny hydrate crystals are present. A different temperature is subsequently selected, and the procedure is repeated to obtain the next incipient hydrate equilibrium point.

Experimental Results and Discussion

In order to establish the validity of the experimental apparatus, six experiments were performed for the propane–water system and the results were compared with the data available in the literature. The numerical values of the measured data and those from the literature are shown in Table I. In Figure 3, the literature data together with the experimental data obtained in this work are shown. The calculated hydrate formation pressures using the method of Englezos and Bishnoi (*6*) are also shown in the figure. There is very good agreement among all the experimental data. It is also noticed that all the predictions are located slightly above the data. The maximum deviation of the experimental

Table I. Experimental Data on Propane Hydrate Formation in Pure Water

T/K	P/MPa			
	this work	literature		
273.70			0.183[b]	
274.15				0.207[c]
274.20	0.208			
274.30		0.207[a]		
274.65				0.232[c]
274.80		0.241[a]	0.232[b]	
274.85				0.239[c]
274.95	0.252			
275.40			0.270[b]	
275.60	0.290			
275.90			0.301[b]	
276.15				0.323[c]
276.25	0.336			
276.40		0.331[a]		
276.75				0.371[c]
277.10			0.386[b]	
277.35	0.435			
277.65				0.455[c]
277.80		0.455[a]		
278.05				0.500[c]
278.15				0.517[c]
278.30	0.545			
278.35				0.542[c]

[a] Robinson and Mehta, 1971. [b] Deaton and Frost, 1946. [c] Kubota et al., 1984.

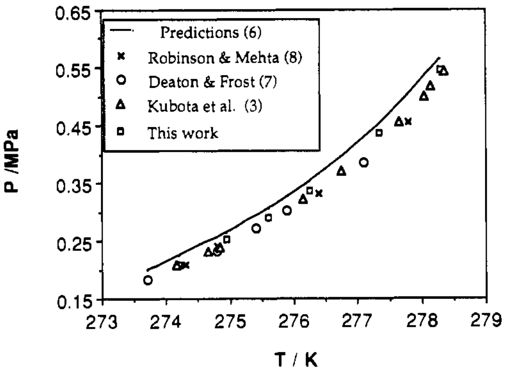

Figure 3. Experimental data and predicted propane hydrate formation pressures in pure water.

data obtained in our equipment and the predictions is 8.0% whereas the average deviation is 5.1%. The maximum deviations between the predictions and the data of Deaton and Frost, Robinson and Mehta, and Kubota et al. are 10.6%, 11.1%, and 8.4%, respectively. The corresponding average deviations are 9.5%, 9.35%, and 5.5%. All these deviations are absolute values. It is also noted that measurements performed at a given temperature were reproducible.

Following the experiments with pure water, a series of experiments with the aqueous electrolyte solutions were performed. The electrolytes used are NaCl, KCl, and $CaCl_2$. First, experiments with a single $CaCl_2$ solution were performed. Subsequently, experiments with the three binary salt solutions and the ternary one were performed. Only one single solution was examined because the main purpose of the study was to obtain hydrate formation data in mixed electrolyte solutions. The selected concentrations fall within the suggested range for using the electrolyte activity coefficient model. The concentrations are relevant to industrial applications and adequate to test the predictive method (*6*). All the experimental data for hydrate formation in the electrolyte solutions are given in Tables II and III. In Figures 4 and 5 these results are given in graphical form. The data obtained in pure water are also given in order to illustrate the inhibiting effect of the electrolytes. It is known that, at a given temperature, the presence of the ions decreases the number of water molecules which are linked with hydrogen bonds. As a result, a higher pressure is required in order to form hydrates (inhibiting effect of electrolytes).

Table II. Experimental Data on Propane Hydrate Formation in Aqueous Electrolyte Solutions

electrolyte (mass %)	T/K	P/MPa
$CaCl_2{\cdot}2H_2O$ (15.00)	268.7	0.205
	269.75	0.270
	270.3	0.317
	271.1	0.376
	271.7	0.412
$CaCl_2{\cdot}2H_2O$ + NaCl (7.50 + 7.50)	265.9	0.172
	266.4	0.186
	267.65	0.248
	268.5	0.312
	269.4	0.385
	269.8	0.418
KCl + NaCl (7.50 + 7.50)	265.2	0.157
	266.2	0.206
	267.45	0.259
	268.5	0.321
	269.05	0.372

Table III. Experimental Data on Propane Hydrate Formation in Aqueous Electrolyte Solutions

electrolyte (mass %)	T/K	P/MPa
$CaCl_2$ + KCl (7.50 + 7.50)	266.3	0.181
	266.9	0.206
	267.5	0.230
	268.1	0.263
	268.55	0.294
	269.5	0.370
	270.1	0.432
$CaCl_2$ + NaCl + KCl (5.00 + 7.50 + 7.50)	261.9	0.172
	262.3	0.192
	262.85	0.214
	263.35	0.249
	263.65	0.267
	264.2	0.286
	264.4	0.303
	264.5	0.303
	265.1	0.342
	265.2	0.352

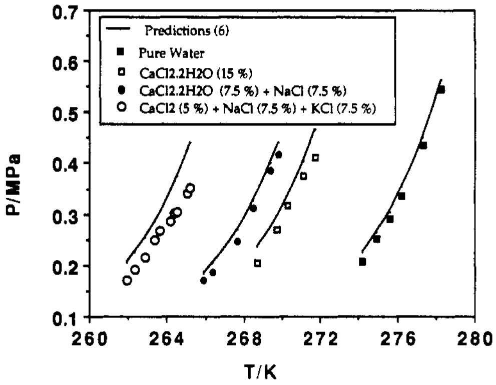

Figure 4. Experimental data and predicted propane hydrate formation pressures in aqueous electrolyte solutions.

The experimental results in Figures 4 and 5 are accompanied with the predictions obtained by using the method of Englezos and Bishnoi (*6*). The agreement between the data for the NaCl + KCl mixture and the predictions, shown in Figure 5, was found to be very good. The maximum and the average absolute deviations between the measured incipient hydrate formation pressures and the predicted ones are 8.0% and 4.9%, respectively. In Figure 4, it is seen that the experimental data in solutions of NaCl and $CaCl_2$ are also in very good agreement with the predicted values. The maximum and the average absolute deviations between the data and the predictions for hydrate formation in the NaCl + $CaCl_2$

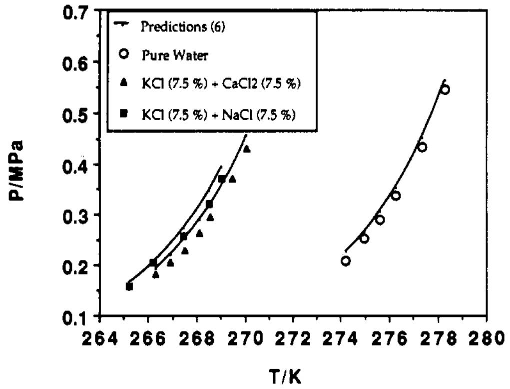

Figure 5. Experimental data and predicted propane hydrate formation pressures in aqueous electrolyte solutions.

solution are 9.7% and 6.5%, respectively. The maximum and average deviations between the data and the predictions concerning hydrate formation in the KCl + $CaCl_2$ solution, shown in Figure 5, are 9.7% and 7.9%. It is seen that the deviations increase slightly when calcium chloride is a constituent of the solutions. The average deviation between the hydrate formation pressures in the single $CaCl_2$ solution and the predicted values is 10.6%. The deviations between the data and predictions were found to be the largest for the ternary solution. The maximum and the average absolute deviations are 25.9% and 20.0%, respectively. One reason for the increase in the magnitude of deviations could be the temperature range of these experiments. In this range, the accuracy of the electrolyte activity coefficient model parameters may be reduced.

Conclusions

An experimental apparatus for the determination of the incipient gas hydrate equilibrium conditions was fabricated and used to obtain equilibrium hydrate formation data for propane in aqueous solutions of NaCl, KCl, and $CaCl_2$ in the temperature and pressure ranges 261.9–278.3 K and 0.157–0.545 MPa. The experimental data were compared with the predictions using the method of Englezos and Bishnoi (*6*) and were found to be in good agreement.

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