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Experimental Investigation of Carbon Dioxide Hydrate Formation Conditions in the Presence of KNO_3, $MgSO_4$, and $CuSO_4$

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Experimental data on the incipient conditions for carbon dioxide hydrate formation in aqueous solutions of KNO_3, $MgSO_4$, and $CuSO_4$ were obtained in the temperature range of (273 to 287) K, in the pressure range of (0.77 to 4.34) MPa, and in salt concentrations ranging from (2.22 to 40.17) mass %. A variable-volume sapphire cell was used for the measurements.

Introduction

Gas hydrates are crystalline compounds of water that are formed from mixtures of water and low molar mass gases at high pressures and low temperatures. The hydrate-forming gases include light alkanes (methane to isobutane), carbon dioxide, hydrogen sulfide, nitrogen, oxygen, xenon, krypton, and chlorine. Through hydrogen bonding, water molecules form a framework containing relatively large cavities that can be occupied by certain gas molecules, which stabilize the structure due to van der Waals forces. Gas hydrates are known to occur in one of four crystal structures: structure I, structure II,[1,2] and structure H[3,4], and a new, as of yet unnamed, structure.[5] Structures I and II consist of two types of cavities, and structure H consists of three types of cavities. The new, and currently unnamed, structure consists of alternating stacks of structure II and structure H hydrates. It has been synthesized by crystallizing choline hydroxide with tetra-*n*-propylammonium fluoride from aqueous solution. Gas hydrates formed from carbon dioxide are known to be structure I.

While gas hydrates have historically been regarded as a nuisance by the petroleum industry, the discovery of huge deposits of gas hydrates in deep-sea sediments and in permafrost has sparked interest in gas hydrates as an unconventional energy source. A cubic meter of hydrate yields about 160 m^3 of gas at standard temperature and pressure and about 0.87 m^3 of water. This relatively high gas density has prompted studies to investigate hydrates as an alternative means to transport and store natural gas. In addition, the use of hydrates for gas storage and transportation is considered a viable option. Gas hydrates, in particular carbon dioxide hydrates, have recently generated considerable interest as a possible means of greenhouse gas sequestration. Concentration of solutions or fruit juices and desalination of seawater with the help of gas hydrates may bring significant energy savings.

To avoid the problems associated with the hydrate formation and to exploit the hydrates as an energy resource or to utilize hydrates to develop new technologies, there is a need to obtain phase equilibrium data and develop prediction methods for pure water as well as for aqueous systems containing inhibitors such as electrolytes. The current study is part of an ongoing experimental and computational program at the University of Calgary dealing with the thermodynamics of gas hydrate formation in aqueous electrolyte solutions, both with and without a nonaqueous cosolvent.[6−18] However, experimental hydrate equilibrium data for carbon dioxide hydrates in aqueous solutions of KNO_3, $MgSO_4$, and $CuSO_4$ have not been reported. Such data could be useful in industrial design applications as well as for testing predictive models. In the present work, experimental three-phase (aqueous liquid solution, vapor, and incipient solid hydrate) equilibrium data for carbon dioxide hydrates in aqueous solutions of KNO_3, $MgSO_4$, and $CuSO_4$ are obtained at temperatures ranging from (273 K to 287) K and at pressures ranging from (0.77 to 4.34) MPa.

Experimental Apparatus and Procedure

The experimental data on hydrate equilibrium data in this work are obtained using the experimental apparatus, and a procedure similar to that described by Dholabhai et al.[6] and Mahadev and Bishnoi.[7] The heart of the apparatus is a high-pressure variable-volume equilibrium cell[12,19,20] made of a sapphire tube (0.75 in. inside diameter × 1.5 in. outside diameter × 4.5 in. long), which is held by top and bottom stainless steel flanges. Three studs are used to keep the tube and the two flanges together. A movable piston that can be moved up and down with a manual gear assembly is used to vary the cell volume. Both the bottom flange and the piston have several junctions for charging the liquid and vapor phases, for the pressure measurement, the vapor phase sampling, and for the introduction of the thermocouple. The thermocouples are calibrated in the range of 263 K to 292 K with a standard deviation of the least-squares fit of 0.09 K. A magnetic stir bar is utilized to mix the liquid cell content driven by a rotating magnet, which is placed below the cell. The cell is immersed into a constant-temperature bath. An ethylene glycol + water solution is used as coolant. The cell pressure is measured with a Rosemount differential pressure (DP) transmitter. The span of the DP is 11 MPa with a combined uncertainty of 0.25% of the span. It is calibrated against a dead weight tester. The cell pressure and the temperatures measured with the DP and the thermocouples, respectively, are sampled at predetermined intervals. They are displayed and stored on a PC using a data logger.

The samples are prepared mass by mass, using a top-loading Mettler balance with a readability of 0.001 g.

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Table 1. Experimental Data on Incipient Carbon Dioxide Hydrate Equilibrium in Aqueous KNO_3, $MgSO_4$, and $CuSO_4$ Solutions

solution composition	T/K	P/MPa	T/K[a]	P/MPa[a]
2.22 mass% KNO_3	275.2	1.83	275.2	1.82
	275.9	2.05	276.1	2.01
	278.2	2.54	278.2	2.53
	278.6	2.79	278.6	2.76
9.26 mass% KNO_3	275.1	2.33	275.2	2.29
	276.1	2.61	276.1	2.57
	277.1	3.02	276.9	2.98
	278.0	3.53	278.1	3.49
15.31 mass % $MgSO_4{\cdot}7H_2O$	275.3	1.85	275.2	1.83
(7.48 wt % $MgSO_4$)	277.2	2.36	277.2	2.33
	278.4	2.91	278.4	2.91
	279.2	3.29	279.2	3.26
	280.3	3.83	280.6	3.83
40.17 mass% $MgSO_4{\cdot}7H_2O$	275.2	2.45	275.1	2.41
(19.63 wt % $MgSO_4$)	276.5	2.96	276.5	2.93
	277.3	3.11	277.3	3.05
	278.1	3.32	278.0	3.28
	278.3	3.60	278.1	3.57
7.47 mass% $CuSO_4$	273.2	1.50	273.4	1.45
	277.3	2.52	277.4	2.49
	280.5	3.86	280.6	3.86
10.68 mass% $CuSO_4$	278.7	2.92	278.7	2.90
	281.4	3.78	281.2	3.76
	277.4	2.40	277.4	2.38
	279.6	3.36	279.6	3.33
12.48 mass% $CuSO_4$	273.9	0.77	273.9	0.73
	278.6	1.97	278.7	1.92
	282.9	3.11	283.1	3.04
	286.1	4.34	286.0	4.32

[a] Data denote the no-hydrate point.

Anhydrous cupric sulfate (Merck, 99.0%), magnesium sulfate, heptahydrate (Merck, 98.0% to 102.0%), and potassium nitrate (Merck, 99.0%) are added to demineralized and twice-distilled water to prepare the respective experimental solutions. The experimental gas, carbon dioxide, with a purity of 99.99% is supplied by PRAXAIR. Table 1 lists the composition of the aqueous solutions.

Prior to each series with a new sample the cell is rinsed several times with distilled water and once with the experimental solution. The whole system is repeatedly flushed with methane. For the experiment, about 15 cm^3 of the sample are introduced into the cell. Three or four equilibrium points are detected for each solution. The "pressure-search" method[10] is used to find the incipient equilibrium point. The hydrates are detected visually. Once the temperature is constant, the corresponding pressure is detected by reducing the pressure range, which includes the equilibrium pressure. The span is defined by two limits where hydrates form and decompose. Setting the new pressure between the limits reduces the range. At the pressures where the hydrates stay stable or deplete, a new upper or lower limit is found. This procedure is repeated until the pressure span is small and only minimal quantity of hydrates is present in the solution. If these conditions remain constant for 3−4 h, they are taken as the equilibrium point. If the remaining hydrates decompose by reducing the pressure by a maximum of 50 kPa, the equilibrium point is considered the incipient hydrate point.

Experimental Results and Discussion

The compositions of the aqueous solutions and the experimental data on CO_2 hydrate formation in pure water, aqueous KNO_3, aqueous $MgSO_4$, and aqueous $CuSO_4$ are given in Table 1. The results are also presented graphically in Figures 1−3. The solid lines shown in the figures are drawn by "visual fit" to clarify the trends of the data. Predictions for CO_2 hydrate equilibrium in pure water, using the Trebble−Bishnoi equation of state[21,22] and the computational procedure given by Clarke et al.,[23] are shown to help estimate the inhibiting effect of each salt. From Figures 1 and 2, it is clear that KNO_3 and $MgSO_4$ have an inhibiting effect on the three-phase equilibrium pressure for CO_2 hydrate formation. However, in Figure 3, it is seen that $CuSO_4$ has an inhibiting effect at lower concentrations and a "promoting" effect at higher concentrations. That is, at high concentrations of $CuSO_4$, the pressure required to form hydrates of CO_2 is less than that required when no salts are present. This behavior has never been reported in the open literature, at the time of this writing. Currently, it is not clear what is responsible for this behavior. It is interesting to note that, at a given temperature, the 10.68% solution is less inhibiting than the 7.47% solution. This suggests that, at a fixed temperature, there is a salt concentration at which the hydrate inhibition is a maxi-

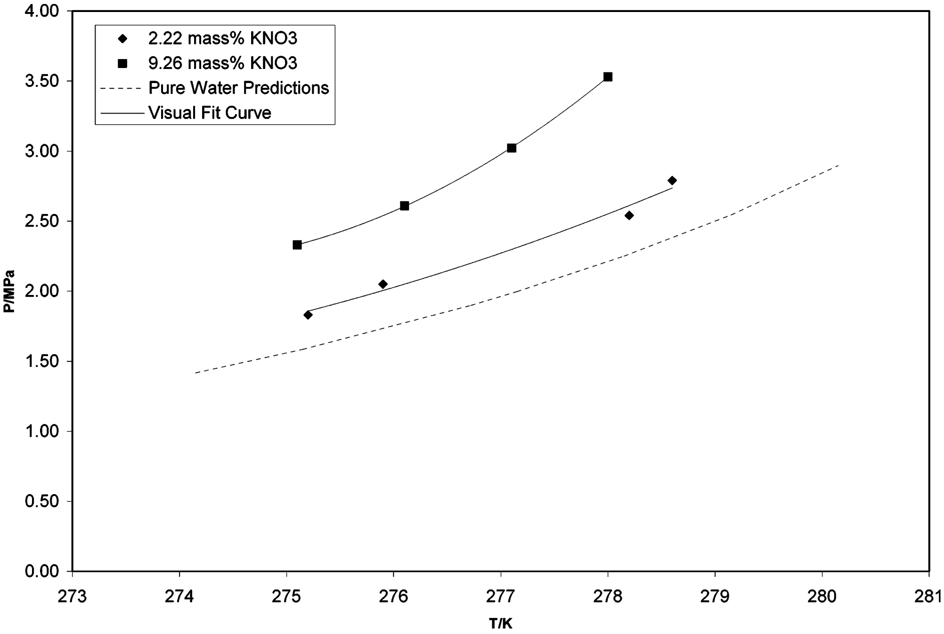

Figure 1. Carbon dioxide hydrate formation pressure as a function of KNO_3 concentration.

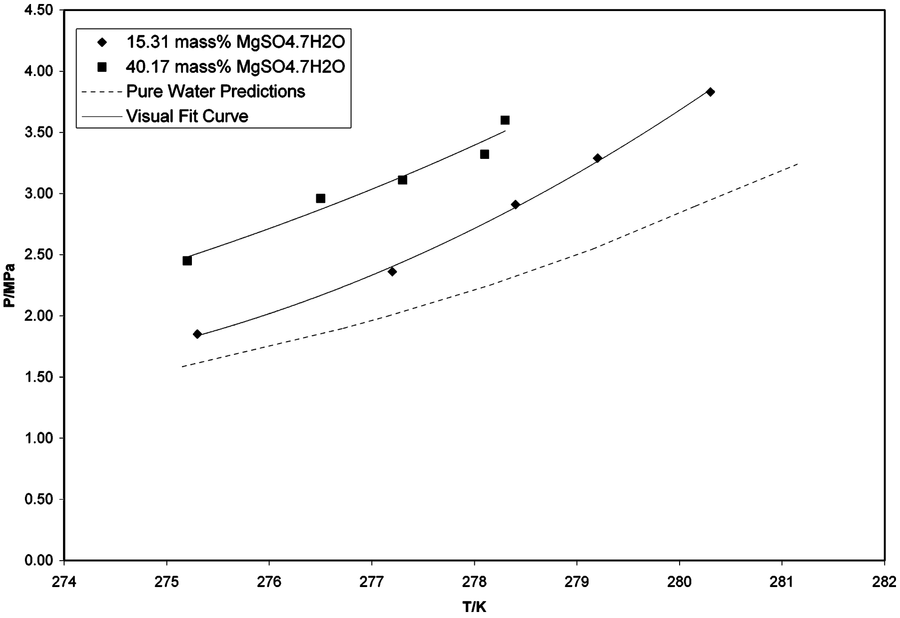

Figure 2. Carbon dioxide hydrate formation pressure as a function of $MgSO_4{\cdot}7H_2O$ concentration.

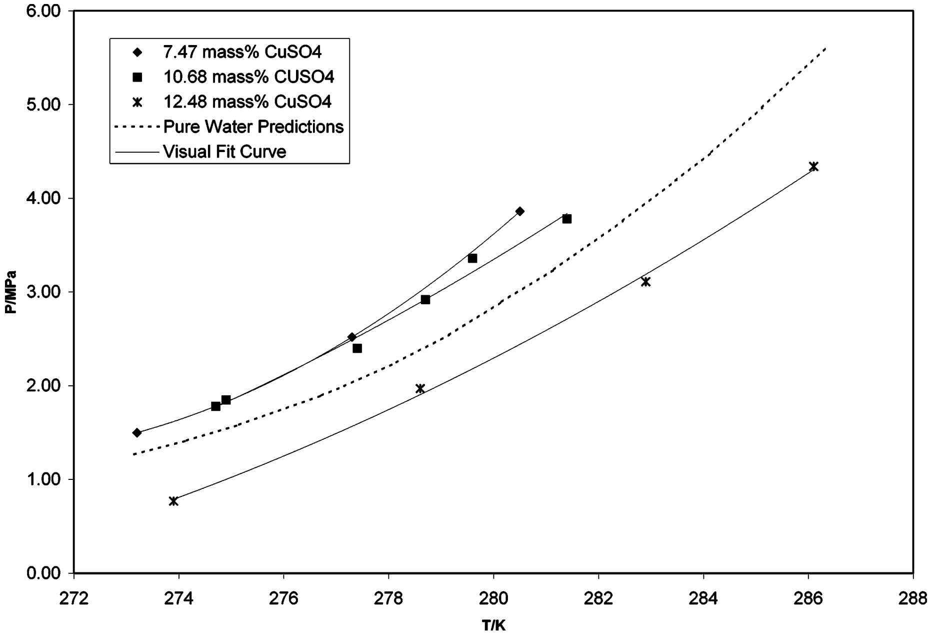

Figure 3. Carbon dioxide hydrate formation pressure as a function of $CuSO_4$ concentration.

mum, and at higher concentrations, the solution becomes less inhibiting and eventually becomes a promoting solution. This may explain the overlap of the 10.68% and 7.47% curves at lower temperatures. This behavior is further noted by the promoting effect seen in the aqueous solution containing 12.48% $CuSO_4$. Further, it was interesting to note that in $CuSO_4$ series, at higher concentrations, the hydrates were not agglomerating and the morphology of the hydrate particles remained apparently granular during the entire formation or decomposition process.

Conclusions

A study was carried out to obtain experimental data for the incipient hydrate formation conditions for CO_2 in aqueous solutions of KNO_3, $MgSO_4$, and $CuSO_4$. The data are obtained in the temperature range of 273 K to 287 K and at pressures ranging from 0.77 MPa to 4.34 MPa. Salt concentrations range from (2.22 to 40.17) mass %. Both $MgSO_4{\cdot}7H_2O$ and KNO_3 are seen to have an inhibiting effect on the formation of CO_2 hydrates, while $CuSO_4$ at high concentrations is seen to have a promoting effect on the formation of CO_2 gas hydrates.

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