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Hydrate Equilibrium Data of Multicomponent Systems in the Presence of Structure-II and Structure-H Heavy Hydrate Formers

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The effect of six newly discovered heavy hydrate-forming compounds on the hydrate phase boundary of a gas mixture, a natural gas, and a model oil has been measured. The study, which is a continuation of a previous work,[1] investigates the effect of cyclopentane, cyclohexane, neopentane, isopentane, methylcyclopentane, and methylcyclohexane at various concentrations. The first three compounds form structure-II hydrates, while the last three compounds are known to promote structure-H hydrates. The experimental hydrate dissociation data have been successfully predicted by the use of a thermodynamic model. The results show that structure-II is the stable hydrate structure for the systems investigated at various heavy hydrate former concentrations (from 0.27 mol % to 59.66 mol %). Also, the structure-II heavy hydrate formers promoted structure-II hydrate formation whereas the structure-H heavy hydrate formers (at the concentrations used) did not change the stable hydrate structure to structure-H and hence inhibited hydrate formation in the above fluid systems. On the basis of the above study, it was concluded that the inclusion of structure-II heavy hydrate formers in the thermodynamic modeling would improve the reliability of hydrate-free zone predictions in real reservoir fluids.

Introduction

Gas hydrates are inclusion compounds in which certain compounds stabilize the cages formed by hydrogen-bonded water molecules under favorable conditions of pressure and temperature. For hydrates to remain stable, a minimum fraction of these cavities have to be filled with guest molecules. The most common hydrate structures are those of structure-I (sI) and structure-II (sII), where each structure is composed of a certain number of large and small cavities formed by water molecules. For a molecule to enter a cavity, its size should be smaller than a certain value. Large molecule guests which can enter only a limited number of large cavities require smaller “help gas“ molecules to mainly fill some smaller cavities sufficiently to stabilize hydrate crystals. Gas hydrates have been reviewed in depth by Sloan.[2]

The current industrial practice in avoiding hydrate problems during oil and gas production is to operate outside the hydrate stability zone. This approach can be made more cost-effective and efficient by reliable determination of the hydrate phase boundary. Experimental determination of the hydrate phase boundary in different production scenarios could be very expensive, so the industrial trend is in favor of improving the predictive methods. The most advanced predictive methods are based on the statistical thermodynamic approach as developed by van der Waals and Platteeuw in 1959.[3] The above approach, combined with a fluid phase behavior model, can be used to predict the hydrate phase boundaries of reservoir fluids in different production scenarios. The main requirements are the optimization of the binary interaction parameters (BIPs) for the phase behavior model and the Kihara parameters[4] for the hydrate model.

In the oil and gas industry, *n*-butane is regarded as the heaviest hydrate-forming compound, and anything heavier than that is regarded as a nonhydrate former. This approach could be adequate for gaseous mixtures. Oil and gas condensate systems, however, contain a significant amount of intermediate/heavy hydrocarbon compounds heavier than *n*-butane with an effective van der Waals’ diameter which theoretically should allow them to enter the large cavities of sII gas hydrates. Furthermore, Ripmeester et al.[5−7] have recently suggested the presence of a third structure, called structure-H (sH), with cavities larger than those of sI and sII. This structure allows the formation of hydrates by even larger molecules in the presence of a help gas. Hydrate-forming compounds heavier than *n*-butane are termed heavy hydrate formers (HHFs).[1] These compounds could be divided into two categories of sII and sH heavy hydrate formers. The former category, which can occupy the large cavity of sII hydrates, contains molecules such as benzene, cyclopentane, cyclohexane, and neopentane. However, the latter, which is suitable for the large cavity of sH hydrates, includes compounds such as isopentane, methylcyclohexane, methylcyclopentane, and adamantane.

While available models can accurately predict the hydrate equilibria for synthetic and simple mixtures, they are generally optimistic, that is, underpredicting the hydrate zone, for oil and rich gas condensates.[8] This could be attributed to the presence of heavy hydrate-forming compounds in the above fluids. These compounds are commonly regarded as nonhydrate formers, so inhibiting hydrate formation. By taking into account the HHFs, a more reliable prediction of the hydrate phase boundary is expected, which is particularly important for oil and gas condensates.

In a previous communication,[1] the effect of small quantities of some of these heavy hydrate formers on the hydrate free zone of a gas mixture and a natural gas was reported. The results showed that sII was the stable hydrate structure. Also, small quantities of sH HHF formers did

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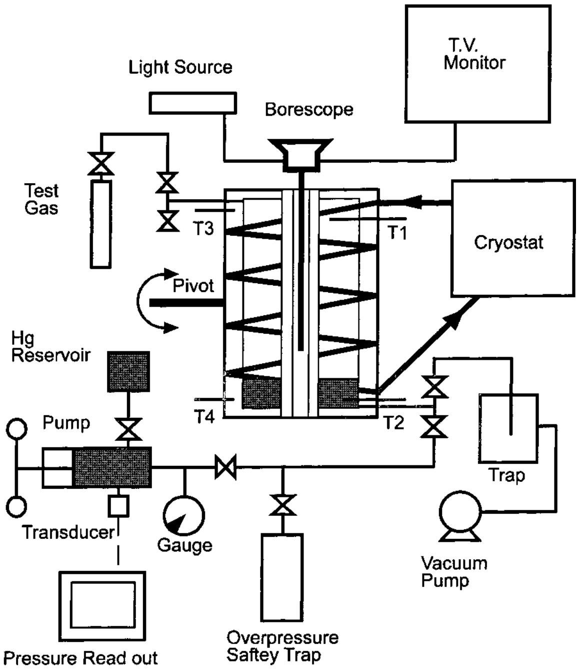

Figure 1. Schematic diagram of hydrate rig.

not change the stable hydrate structure and hence did not have a significant effect on the hydrate phase boundary. However, sII HHFs had a significant impact on the hydrate phase boundary of the gas systems mentioned earlier, even in small concentrations. The results showed that sII HHFs should be included in the thermodynamic modeling for reliable predictions, whereas sH HHFs could be safely ignored for the hydrate free zone calculations.

The present work is a continuation of the above work where the effect of high concentrations of sII and sH HHFs on the hydrate free zone of several synthetic and real systems has been investigated. In this study, several HHFs, that is, cyclopentane, cyclohexane, neopentane, isopentane, methylcyclopentane, and methylcyclohexane have been added to a gas mixture, a natural gas, and a model oil system. The hydrate free zones of the above systems, with and without HHFs, have been measured, identifying the hydrate characteristics of high concentrations of HHFs in multicomponent systems. The experimental data have been successfully compared with the predictions of an in-house thermodynamic model.

It should be noted that, in this work, the identification of a stable hydrate structure is based on thermodynamic modeling and comparison with experimental hydrate dissociation data. A final proof for the stable hydrate structure requires direct measurements by suitable physical techniques (e.g., NMR, X-ray, or Raman spectroscopy).

Experimental Section

Test Facility. The experiments were performed in a high-pressure hydrate rig the layout of which is shown in Figure 1. The hydrate cell consisted of a metal body inside which an optically clear quartz glass tube was housed. The maximum effective volume of the cell was 540 cm^3, and the maximum working pressure was 69 MPa. The effective volume was adjusted by injecting or withdrawing mercury. The temperature of the cell was controlled by circulating coolant round a jacket surrounding the cell. The cell was mounted on a pivot, and mixing was obtained by rocking the cell. The pressure and temperature of the system were sampled and recorded at regular intervals. The temperature of the bath was programmed and controlled by a computer. To view the cell contents, a borescope could be passed into the quartz glass tube. A detailed description of the experimental setup has been given elsewhere.[9] The estimated accuracy of temperature and pressure in the experiments was ±0.1 K and ±7 kPa, respectively.

Table 1. Composition (mol %) of the Natural Gas, the Gas Mixture, and the Two Batches of the Model Oil

component	natural gas	gas mixture	model oil (1st batch)	model oil (2nd batch)
N_2	4.99			
CO_2	1.12			
C_1	86.36	92.18	26.52	26.89
C_2	5.43	6.33	3.89	3.91
C_3	1.49	1.49	8.79	7.58
i-C_4	0.18			
n-C_4	0.31			
i-C_5	0.06			
n-C_5	0.06		11.36	11.93
C_6^+	<0.01			
n-C_{10}			49.44	49.69

Test Fluids. The gases used in this work were all high purity purchased from commercial suppliers. The details of all the fluids are documented below. Distilled water was used in all tests.

nitrogen	99.99% pure
methane	instrument grade, 99.9% pure
ethane	99.9% pure
propane	instrument grade, 99.5% pure
neopentane	100.00% pure
n-pentane	99+% pure
isopentane	99.5+% pure
n-decane	99+% pure
cyclopentane	99+% pure
cyclohexane	99+% pure
methylcylohexane	99+% pure
methylcyclopentane	98% pure

The compositions of the gas mixture and model oil are presented in Table 1. The gas mixture and the model oil were prepared from the individual components gravimetrically. Natural gas was purchased from BOC, and the composition was analyzed by gas chromatography (Table 1). The compositions of the synthetic gas mixture and the model oil were adjusted to match typical hydrate phase boundaries of similar real systems.

Procedure. To determine the hydrate dissociation point, the cell was charged with water (approximately 20 g) and the test fluid, and the temperature was lowered until hydrates were formed. The temperature was then raised stepwise allowing sufficient time (4 h) at each step for equilibrium to be achieved.[10,11] At temperature steps below the dissociation point, some hydrates were decomposed where the released gas raised the pressure markedly. Once the temperature was above the dissociation point, with no more hydrates to decompose, the pressure rise was quite small. A plot of the pressure versus temperature would therefore give two distinct lines of different slopes, with the break over at the dissociation point.[9]

Thermodynamic Modeling

The thermodynamic model is detailed elsewhere.[12] The model uses a single cubic equation of state (EoS) to describe all the fluid phases and solid solution theory for hydrate phases.[3] The model uses the general multiphase flash routine,[13] which enables it to perform hydrate point calculations as well as flash calculations in the presence of gas hydrates with any number of phases. In the modeling of the saline water system, the EoS is combined with the

Table 2. Dissociation Points for Hydrates Formed from Natural Gas and Natural Gas with Small Concentrations of sII and sH Heavy Hydrate Formers

T/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.07)
Natural Gas		Natural Gas with 0.43 mol % Cyclopentane	
Moles Water/Moles Hydrocarbon = 3.028		Moles Water/Moles Hydrocarbon Not Measured	
276.1	1.269	283.1	1.255
284.1	3.337	284.9	2.027
290.0	7.619	288.9	3.144
Natural Gas with 1.02 mol % Cyclohexane		Natural Gas with 0.68 mol % Methylcyclopentane	
Moles Water/Moles Hydrocarbon = 13.689		Moles Water/Moles Hydrocarbon Not Measured	
277.1	1.110	278.5	1.717
280.4	1.751	284.8	3.647
285.0	3.137	289.4	7.019
289.2	5.654		
Natural Gas with 0.27 mol % Cyclohexane			
Moles Water/Moles Hydrocarbon = 8.296			
278.5	1.531		
283.2	2.806		
287.9	5.095		
292.1	9.639		

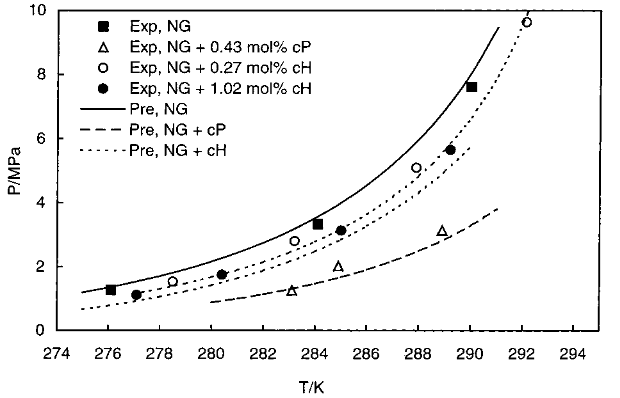

Figure 2. Experimental and predicted effect of cyclopentane (cP) and cyclohexane (cH), respectively, on the hydrate free zone of the natural gas (NG).

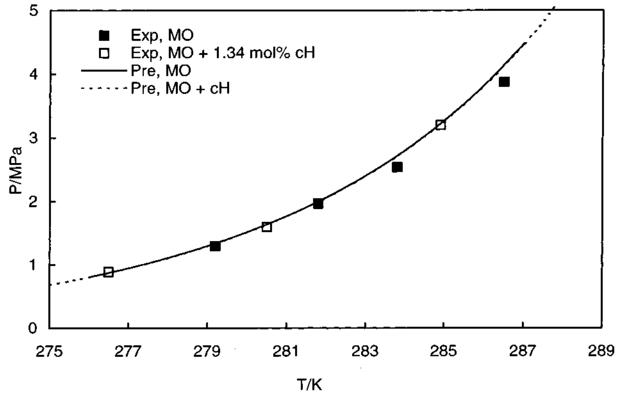

Figure 3. Experimental and predicted effect of 1.34 mol % cyclohexane (cH) on the hydrate free zone of the first batch model oil (MO).

Debye−Hückel electrostatic term to take into account the effect of salts.[12] The modeling of the individual HHFs is detailed in previous communications.[9,14−17]

Results and Discussions

Structure-II Heavy Hydrate Formers (sII HHFs). The effect of small concentrations of sII HHFs on the hydrate phase boundary of a natural gas (with composition in Table 1) has been discussed in a previous communication.[1] Table 2 presents the hydrate dissociation of the natural gas and the natural gas with 0.27 mol % and 1.02 mol % cyclohexane as well as 0.43 mol % cyclopentane. At the test conditions, the natural gas/cyclopentane and the natural gas/0.27 mol % cyclohexane systems were in the three-phase region with water (L_1), hydrate (H), and vapor (V) in equilibrium, whereas the natural gas/1.02 mol % cyclohexane system was in the four-phase region of water (L_1), hydrate (H), vapor (V), and liquid hydrocarbon (L_2). Figure 2 presents the hydrate phase boundary of the natural gas in the presence of the two sII HHFs. As shown in the figure, sII HHFs promote hydrate formation even at small quantities. Interestingly, the increase in cyclohexane concentration from 0.27 mol % to 1.02 mol % did not change the hydrate phase boundary significantly, due to the formation of a liquid hydrocarbon phase. The predictions by the thermodynamic model are also shown in the figure, and good agreement between the experimental data and the model is demonstrated.

The five-component model oil was prepared to study the effect of sII HHFs on the hydrate phase boundary of oil systems. Three series of tests were carried out using the model oil (the first batch) with a composition as shown in Table 1. The aim of the first series was to establish the hydrate phase boundary of the model oil. The objective in the second and third series was to investigate the effect of small concentrations of cyclohexane and cyclopentane on the hydrate phase boundary of the model oil, respectively. The dissociation points for these three sets of tests are presented in Table 3.

Figures 3 and 4 show the hydrate phase boundaries of the model oil with 1.34 mol % cyclohexane and the model oil with 1.54 mol % cyclopentane, respectively. As can be seen, the addition of 1.34 mol % cyclohexane had no significant effect on the phase boundary of hydrates formed from the model oil. The addition of 1.54 mol % cyclopentane shifted the phase boundary by about 1.3 K at 2 MPa.

The in-house computer model was used to predict the hydrate phase boundaries of the model oil, model oil with 1.34 mol % cyclohexane, and model oil with 1.54 mol % cyclopentane. It should be noted that, at the test conditions, all of the above systems were in the four-phase L_1-L_2-H-V region. Also, it was assumed that hydrate sII is the stable hydrate structure. The predicted hydrate phase boundaries of the above systems are also presented in Figures 3 and 4.

A second batch of the model oil (with composition similar to the first batch) was prepared to investigate the effect of high concentrations of sII HHFs on the hydrate phase boundary of the model oil. Table 1 shows the composition of the second batch of the model oil. Table 4 presents the measured hydrate phase boundaries of the model oil

Table 3. Dissociation Points for Hydrates Formed from Model Oil, Model Oil with 1.34 mol % Cyclohexane, and Model Oil with 1.54 mol % Cyclopentane (First Batch)

model oil		model oil with 1.34 mol % cyclohexane		model oil with 1.54 mol % cyclopentane	
T/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)
279.2	1.296	276.5	0.889	279.7	1.062
281.8	1.965	280.5	1.600	282.7	1.834
283.8	2.537	284.9	3.199	285.9	2.972
286.5	3.875			287.9	4.275

Table 4. Dissociation Points for Hydrates Formed from Model Oil with 17.87 mol % Cyclopentane, Model Oil with 16.77 mol % Neopentane, and Model Oil with 10.35 mol % Cyclopentane and 9.88 mol % Neopentane (Second Batch)

model oil with 17.87 mol % cyclopentane		model oil with 16.77 mol % neopentane		model oil with 10.35 mol % cyclopentane and 9.88 mol % neopentane	
T/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)
278.0	0.276	278.7	0.993	278.5	0.483
282.6	0.786	282.2	1.724	283.3	1.200
287.9	1.834	286.7	3.420	288.2	2.634

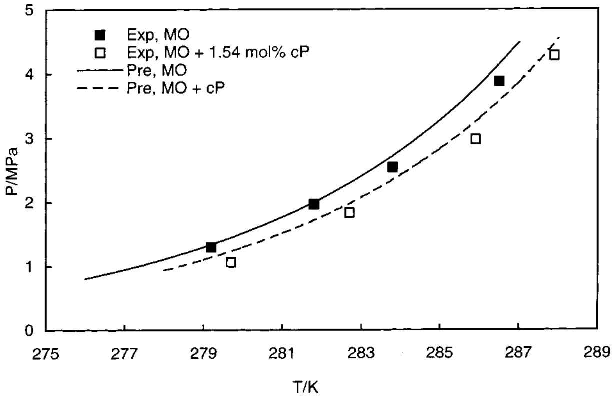

Figure 4. Experimental and predicted effect of 1.54 mol % cyclopentane (cP) on the hydrate free zone of the first batch model oil (MO).

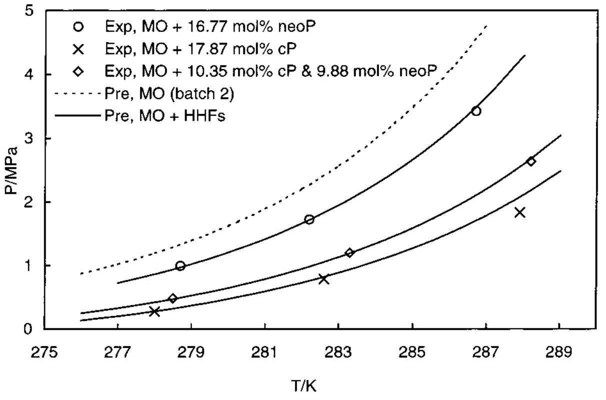

Figure 5. Experimental and predicted effect of 17.87 mol % cyclopentane (cP), 16.77 mol % neopentane (neoP), and 10.35 mol % cP and 9.88 mol % neoP, respectively, on the hydrate free zone of the second batch model oil (MO).

(second batch) with 17.87 mol % cyclopentane, model oil with 16.77 mol % neopentane, and model oil with 10.35 mol % cyclopentane and 9.88 mol % neopentane.

Another objective of the above tests was to examine the reliability of the thermodynamic model in predicting the hydrate phase boundary of the model oil when high concentrations of sII HHFs are present (causing a significant shift in the hydrate phase boundary). The last set of tests was designed to validate the thermodynamic model against independent experimental data, when a mixture of the newly discovered heavy hydrate formers is present.

Figure 5 presents the experimental hydrate dissociation conditions for the model oil (second batch) with added cyclopentane and neopentane. In the figure the predicted hydrate phase boundaries for the model oil, as well as the model oil with added HHF, are presented. Excellent agreement is observed between the experimentally determined and the predicted hydrate phase boundaries. Cyclopentane is seen to be a stronger hydrate former than neopentane and cyclohexane, as shown in Figure 5. The combined hydrate promotion effect of cyclopentane and neopentane on the model oil is also shown in Figure 5. Again there is a good agreement between the thermodynamic model predictions and the experimental data, demonstrating the reliability of the thermodynamic modeling in predicting the combined effect of mixed HHFs.

Similar to the previous set of data, the above systems were in the four-phase L_1-L_2-H-V region. It was assumed that sII was the stable hydrate structure in all cases. This was confirmed by the excellent agreement between experimental data and the predictions of the thermodynamic model. The above results showed that the addition of sII HHFs could promote hydrate formation in most cases (as they do in gas systems, reported in a previous communication[1]). The nature and magnitude of their impact depends on the hydrate phase boundary of the original fluid and the type and concentration of the HHF (e.g. the addition of weak sII HHFs such as benzene may shift the hydrate phase boundary of some reservoir fluids to higher pressures). However, in real reservoir fluids where the sII HHFs do exist naturally, their exclusion from the hydrate phase behavior calculations could result in unreliable predictions.

Structure-H Heavy Hydrate Formers (sH HHFs). Tohidi et al.[1] showed that although sH HHFs generally promote hydrate formation in methane and nitrogen systems, they do not have a significant effect on the hydrate phase boundary of gaseous systems at low concentrations. Table 2 presents the hydrate dissociation points for the gas mixture in the presence of 0.68 mol % methylcyclopentane. At the test conditions, the system was in the four-phase L_1-L_2-V-H region. Figure 6 shows the above measurements together with those of the natural gas and predicted hydrate phase boundaries, assuming sII and sH hydrates. The good agreement between the experimental data and the predicted sII hydrate phase boundary shows that 0.68 mol % methylcyclopentane cannot change the stable hydrate structure to sH. In this work the effect of high concentrations of sH HHFs on the hydrate phase boundary of a gas mixture has been studied.

The three-component gas mixture was prepared with composition as reported in Table 1. Four series of tests were conducted to determine the hydrate phase boundary of the

Table 5. Dissociation Points for Hydrates Formed from Gas Mixture, Gas Mixture with 23.14 mol % Methylcyclohexane, Gas Mixture with 23.48 mol % Methylcyclopentane, and Gas Mixture with 59.66 mol % Isopentane

gas mixture		gas mixture with 23.14 mol % methylcyclohexane		gas mixture with 23.48 mol % methylcyclopentane		gas mixture with 59.66 mol % isopentane	
T/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)	*T*/K (±0.1)	*P*/MPa (±0.007)
276.5	1.455	280.0	2.613	278.7	2.089	275.8	2.075
283.6	3.116	284.9	4.757	283.4	3.861	278.8	3.247
290.6	7.963	288.5	8.184	288.3	7.791	282.2	5.143

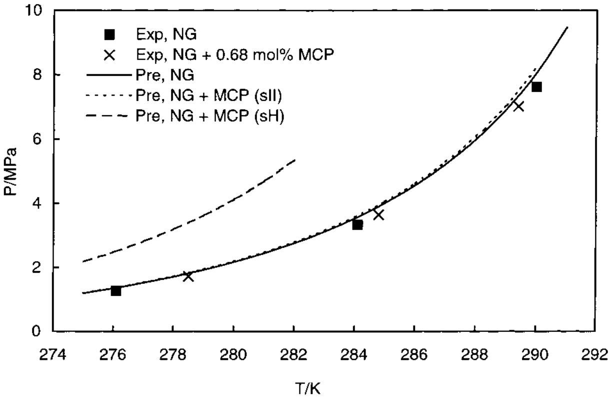

Figure 6. Experimental and predicted effect of methylcyclopentane (MCP) on the hydrate free zone of the natural gas (NG).

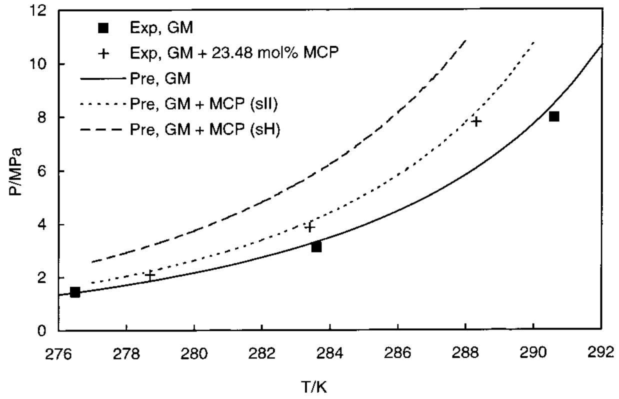

Figure 8. Experimental and predicted effect of methylcyclopentane (MCP) on the hydrate free zone of the ternary gas mixture (GM).

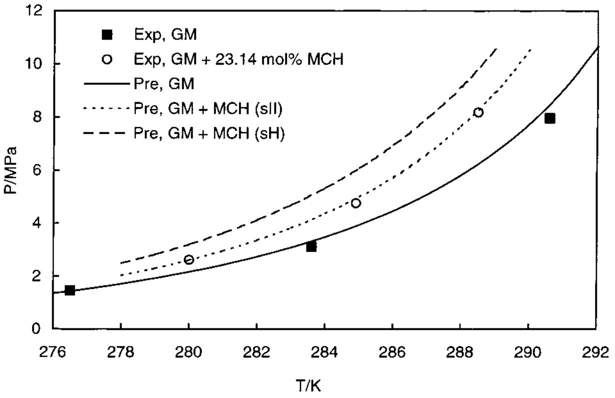

Figure 7. Experimental and predicted effect of methylcyclohexane (MCH) on the hydrate free zone of the ternary gas mixture (GM).

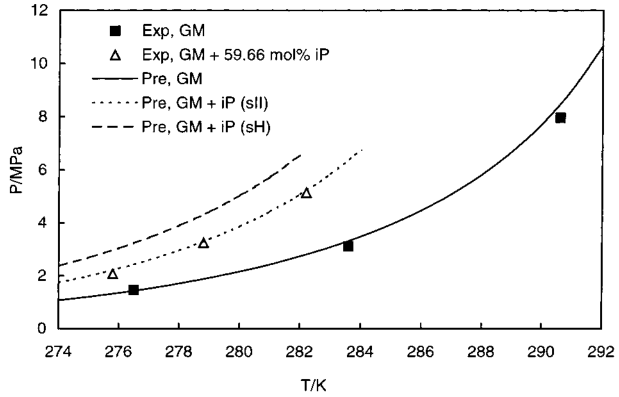

Figure 9. Experimental and predicted effect of isopentane (iP) on the hydrate free zone of the ternary gas mixture (GM).

gas mixture with and without three sH HHFs. Methylcyclohexane, methylcyclopentane, and isopentane were chosen to represent sH HHFs. Table 5 presents the hydrate phase boundaries of the gas mixture, the gas mixture with 23.14 mol % methylcyclohexane, the gas mixture with 23.48 mol % methylcyclopentane, and the gas mixture with 59.66 mol % isopentane.

The in-house thermodynamic model was used to predict the hydrate phase boundary of the gas mixture with and without the above sH HHFs. It should be noted that, with the exception of the gas mixture, which is in the three-phase L_1−H−V region, all other systems are in the four-phase L_1−L_2−H−V region. To determine the stable hydrate structure at high concentrations of sH HHFs, the hydrate phase boundaries assuming sII and sH were calculated. Figures 7−9 show the experimental and predicted hydrate phase boundaries of the gas mixture in the presence of methylcyclohexane, methylcyclopentane, and isopentane, respectively. As shown in the figures, the predicted hydrate phase boundaries for sII hydrates are in excellent agreement with the experimental data. The predicted phase boundaries for sH hydrates are at significantly higher pressures than those of sII hydrates. The results show that although high concentrations of sH HHFs formers (for the compounds investigated) do not change the stable hydrate structure from sII to sH, they inhibit sII hydrate formation in the gas mixture. The good agreement between experimental data and thermodynamic modeling confirms the previous findings that sH HHFs do not take part in hydrate formation in the systems investigated. It is, however, possible to change the stable hydrate structure to sH by further increasing the concentration of sH heavy hydrate formers. However, it is unlikely that such a system could be found in real reservoir fluids.

Conclusions

The effect of the newly discovered heavy hydrate formers (hydrate-forming compound heavier than *n*-butane) on the hydrate phase boundary of a ternary gas mixture, a natural gas, and a model oil was investigated. In this study, which was a continuation of a previous work, three structure-II and three structure-H heavy hydrate formers (HHF) were studied. The main objectives of this work were (a) the impact of heavy hydrate formers on oil systems; (b) the effect of high concentrations of HHFs on the stability of hydrate structures; and (c) the generation of data on systems involving heavy hydrate formers for optimization and validation purposes. The results and conclusions can be summarized as follows:

(1) The predictions of an in-house thermodynamic model were compared with the independent experimental data generated in this work. The results showed that the thermodynamic model is capable of predicting the hydrate free zones of the fluid systems in the presence of various concentrations and mixtures of heavy hydrate formers.

(2) Structure-II is the stable hydrate structure for all the systems investigated.

(3) Some structure-II heavy hydrate formers can have a significant effect on the hydrate phase boundary of oil systems at high concentrations.

(4) Structure-H heavy hydrate formers, even at high concentrations did not change the stable hydrate structure for the systems investigated.

(5) Structure-H heavy hydrate formers do not take part in hydrate formation in the multicomponent systems investigated, hence, inhibiting hydrate formation.

(6) The results of this limited study have shown that there is no need to model the hydrate characteristics of structure-H heavy hydrate formers for predicting the hydrate free zones of the systems investigated.

(7) On the basis of the results of this study, the modeling of structure-II heavy hydrate formers is recommended for improving the reliability of hydrate free zone prediction.

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