

Experimental Determination and Modeling of Methane Hydrates in Mixtures of Acetone and Water

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In this article, experimental data on methane hydrate formation in mixtures of water and acetone are presented. For eight different acetone–water mixtures, the phase transition hydrate + liquid + vapor → liquid + vapor (HLV → LV) was determined in the pressure range $2.50 < p/\text{MPa} < 11.25$. In addition, the experimental data obtained were described by a model that takes into account the variation of the enthalpy of hydrate formation as a function of pressure and acetone concentration. The average absolute temperature difference in the representation of the hydrate formation temperatures of methane in the presence of acetone is less than 0.32 K.

Introduction

In earlier investigations by Heng-Joo Ng and Robinson (1994), rather unexpectedly it was found that, depending on its concentration, acetone may promote or suppress the formation of methane hydrate. At lower concentrations acetone acts as a hydrate promoter, whereas at higher acetone concentrations this compound suppresses the formation of methane hydrate. Although measurements on the methane hydrate formation in mixtures of acetone and water have been reported before by Heng-Joo Ng and Robinson (1994), it was decided to repeat the measurements.

To model the experimental data obtained, the thermodynamic model originally proposed by Pieroen (1955) and again applied by Moshfeghian and Maddox (1993) was used. This model has proven to be able to accurately predict hydrate formation conditions in the presence of compounds such as methanol and ethylene glycol. In this study the capability of the model has been extended to predict hydrate formation temperatures of methane in mixtures of acetone and water. The model takes into account the variation of the enthalpy of hydrate formation due to pressure and acetone concentration.

Experimental Section

The experimental work was carried out in a Cailletet apparatus that has already been described before in literature by, for instance, Peters et al. (1993). Also the experimental procedures have previously been described by Coorens et al. (1988). In this study, for each filling the phase transition HLW → LV was determined at eight different pressures; namely, 2.50, 3.75, 5.00, 6.25, 7.50, 8.75, 10.00, and 11.25 MPa. At fixed pressure, the temperature was measured at which the last tiny crystal of hydrate disappeared. The accuracy of the measurement of the temperature at which the phase transition HLW → LV occurred was within ± 0.1 K.

In Table 1 the suppliers and the purity claimed by the suppliers of the chemicals used in this study are sum-

Table 1. Suppliers and Purity of the Pure Substances Used

substance	supplier	purity in mol %
methane	Air Products	99.995
acetone	Baker	99.0
water		double distilled

marized. All substances were used without further purification.

Modeling

In this study the thermodynamic model, originally proposed by Pieroen (1955) and reintroduced by Moshfeghian and Maddox (1993) to predict accurately hydrate formation temperatures in the presence of hydrate suppressants such as methanol and ethylene glycol, was applied. It was shown that the model covers a wide range of pressure and suppressant concentration. The model reads

$$\ln a_w = -\frac{\Delta H}{nR} \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (1)$$

In this equation a_w is the activity of water ($a_w = x_w \gamma_w$), ΔH the enthalpy of hydrate formation, T the hydrate formation temperature in the presence of a suppressant, T^0 the hydrate formation temperature of pure water, and R the universal gas constant. In eq 1, the temperature T^0 is calculated from the Parrish and Prausnitz (1972) or the Holder et al. (1980) model. The hydrate formation temperature in the presence of acetone is obtained from eq 1. This equation expects as input the activity $a_w = x_w \gamma_w$ of water, which was calculated from the Van Laar equation. Its parameters were obtained by fitting VLE data of the system acetone + water to this model. For the activity coefficient γ_w of water the following expression was obtained:

$$\ln \gamma_w = 1.656 \left(1 + \frac{1.656 x_w}{1.900 x_a} \right)^{-2} \quad (2)$$

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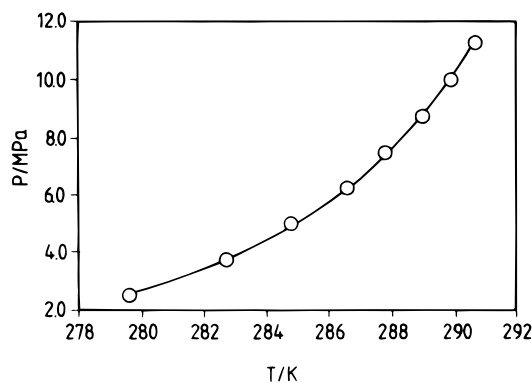


Figure 1. P,T diagram of hydrate formation in the system methane-acetone-water (mole fraction of acetone $x_a = 0.0167$). Open circles, experimental data; full curve, modeling.

Table 2. Experimental Results of the Phase Transition HLV \rightarrow LV ($x =$ Mole Fraction Acetone)

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
$x = 0.0167$		$x = 0.0721$		$x = 0.2755$	
279.6	2.50	281.5	2.50	275.6	2.50
282.7	3.75	284.4	3.75	278.8	3.75
284.8	5.00	286.5	5.00	280.9	5.00
286.6	6.25	288.1	6.25	282.6	6.25
287.8	7.50	289.4	7.50	284.1	7.50
289.0	8.75	290.4	8.75	285.2	8.75
289.9	10.00	291.4	10.00	286.2	10.00
290.7	11.25	292.1	11.25	287.1	11.25
$x = 0.0333$		$x = 0.0936$		$x = 0.4769$	
281.4	2.50	281.1	2.50		
284.2	3.75	284.0	3.75	274.2	3.75
286.3	5.00	286.1	5.00	276.6	5.00
287.9	6.25	287.6	6.25	278.6	6.25
289.3	7.50	288.9	7.50	280.2	7.50
290.3	8.75	290.0	8.75	281.5	8.75
291.2	10.00	290.9	10.00	282.6	10.00
292.1	11.25	291.7	11.25	283.7	11.25
$x = 0.0528$		$x = 0.1437$			
281.7	2.50	279.5	2.50		
284.6	3.75	282.5	3.75		
286.7	5.00	284.6	5.00		
288.3	6.25	286.1	6.25		
289.6	7.50	287.5	7.50		
290.6	8.75	288.6	8.75		
291.5	10.00	289.5	10.00		
292.3	11.25	290.3	11.25		

In this equation, x_w and x_a represent the mole fractions of water and acetone respectively in the liquid phase.

The enthalpy of hydrate formation was obtained by fitting all the experimental hydrate formation values to an empirical model, with the exception of values at $x_a = 0.1437$. The following correlation was obtained:

$$\frac{\Delta H}{nR} = \frac{-31.3 - (3.0 \times 10^3)x_a - (3.7 \times 10^5)x_a^{4.5} + (3.36 \times 10^8)x_a^{13.5}}{1 - (9.3 \times 10^{-2}) \ln(p/p^0)} \quad (3)$$

In eq 3, p represents the pressure in kPa and $p^0 = 1$ kPa.

Results

In the pressure range $2.50 < p/MPa < 11.25$, for eight different acetone-water mixtures (1.67, 3.33, 5.28, 7.21, 9.36, 14.37, 27.55, and 47.69 mol % acetone) the phase transition HLV \rightarrow LV was determined experimentally. In Table 2 the data are summarized. Figure 1 shows the experimental results for the lowest acetone concentration (1.67 mol %), while Figure 2 shows the results for the acetone concentration of 27.55 mol %. In Figure 3 the eight

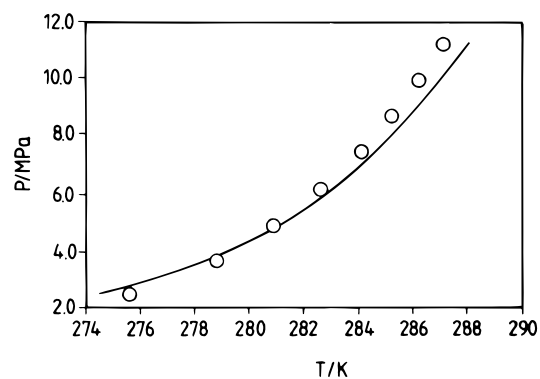


Figure 2. P,T diagram of hydrate formation in the system methane-acetone-water (mole fraction of acetone $x_a = 0.2755$). Open circles, experimental data; full curve, modeling.

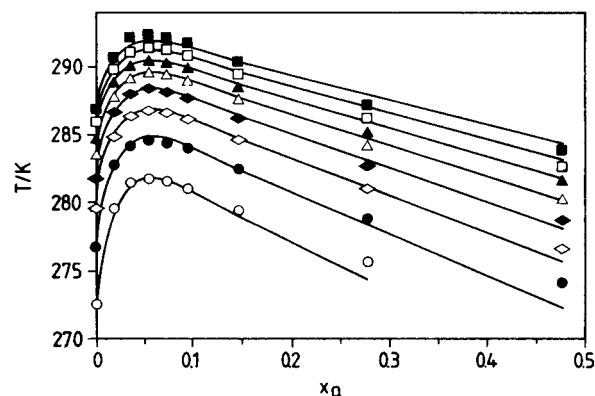


Figure 3. T,x_a representation of the experimental data (symbols) and modeling results. From lower to higher temperatures the sequence of the pressures of the eight isobars are 2.50, 3.75, 5.00, 6.25, 7.50, 8.75, 10.00, and 11.25 MPa (x_a is mole fraction of acetone).

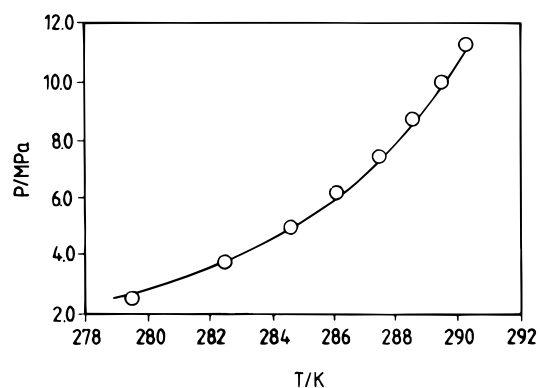


Figure 4. P,T diagram of hydrate formation in the system methane-acetone-water (mole fraction of acetone $x_a = 0.1437$). Open circles, experimental data; full curve, model predictions.

isobars obtained are shown graphically. A comparison of the data obtained in this investigation with those reported earlier in literature by Heng-Joo Ng and Robinson (1994) shows excellent agreement.

The ability of the model proposed in predicting hydrate formation temperatures in acetone-water mixtures was tested by calculating these temperatures for the mixture in which data were not used to correlate the parameters in the model, i.e., $x_a = 0.1437$. Figure 4 shows the predictions.

Discussion

This investigation confirmed the earlier findings of Heng-Joo Ng and Robinson (1994). Figure 3 clearly shows that,

at acetone concentrations lower than 5 mol %, for all isobars the hydrate formation temperatures are substantially higher compared to those of pure water. However, at acetone concentrations higher than 5 mol %, the hydrate formation temperatures for all isobars tend to decline with the acetone concentration. Consequently, it becomes apparent that acetone present in concentrations lower than 5 mol % is a hydrate-promoting agent, whereas at concentrations higher than 5 mol % acetone shows suppressing capabilities. A molecular explanation for this behavior is still lacking.

From the modeling results it became apparent that the average absolute deviation (AAD) in the hydrate formation temperatures for the acetone concentration not used for the parameter correlation ($x_a = 0.1437$) is 0.22 K. On the other hand, the AAD in the data used for the parameter fitting is less than 0.32 K, i.e., the model has predictive capabilities for the dualistic behavior of acetone on the methane hydrate formation.

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