Experimental Measurement and Modeling of R22 (CHClF₂) Hydrates in Mixtures of Acetone + Water

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The effect of acetone on R22 (CHClF₂) hydrate equilibrium conditions was investigated. A full view equilibrium cell and associated equipment were designed, fabricated, and used for this purpose. Adding acetone caused an increase in the equilibrium pressure. The investigated mole fractions of acetone in water were 0.02, 0.04, and 0.06. The equilibrium conditions were measured in the pressure range 0.223 to 0.704 MPa. In contrast to methane hydrate in the presence of acetone, the system of R22 + water + acetone showed an inhibition effect for all of the above concentrations of acetone. The existing model for structure II hydrates in the ternary mixtures of methane + water + acetone was applied to the system R22 + water + acetone. The measured dissociation temperatures were compared with the model prediction.

Introduction

Gas hydrates (or clathrate hydrates) are icelike crystalline compounds formed from water and small gas molecules such as methane and nitrogen. Within the hydrate lattice, water molecules form a network of hydrogen bonded cagelike cavities that host the small "guest" gas molecules which are required to stabilized the structure. The resulting crystalline structures thermodynamically are solid solutions.

Some aqueous solutions containing organic solutes such as 1,4-dioxane and acetone act as a methane hydrate promoter at concentrations not exceeding 0.06 mole fraction of acetone. At higher concentrations, this effect gradually changes and the organic eventually becomes a hydrate inhibitor.[1−4] The promotion effect of these water−solute hydrate formers has been investigated because it is suggested that these compounds can be used to store natural gas in a stabilized gas hydrate under more feasible conditions.[2]

In this work, the effect of acetone on the R22 hydrate equilibrium is investigated. The objective of this study is to determine the three phase equilibrium, hydrate−aqueous solution−vapor, of R22 hydrate in the presence of water + acetone.

The model developed by Javanmardi et al.[4] for structure II hydrates in the ternary mixtures of methane + water + acetone has been extended to the system R22 + water + acetone. The chemical potential of the hydrate phase and the water activity have been represented using the van der Waals and Platteeuw theory[5] and the van Laar free energy model, respectively.

Experimental Section

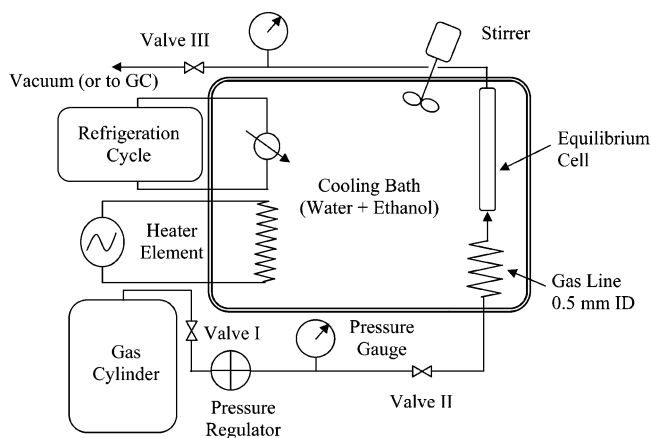**Materials.** The R22 gas was supplied by Rhodia Chemical Co, with purity equal to 99.8 mol % (at least). Double distilled water was used for preparing the required solutions. Acetone with a minimum purity equal to 99.0% was supplied by Merck Chemical Co.

Apparatus. A full view of the equilibrium cell and associated equipment is shown schematically in Figure 1. The equilibrium cell primarily consists of a constant-volume glass tube (1.2 cm i.d. × 1.8 cm o.d. × 34 cm), as shown in Figure 2. The glass tube is sealed at either end with conical O-rings. The total internal volume of the equilibrium cell is about 80 cm³. The maximum safe pressure of the cell is 1.400 MPa. The equilibrium cell is immersed in a cooling bath of about 40 L of refrigerated water−ethanol solution.

As shown in Figure 1, the hydrate former stored in a gas cylinder is injected into the equilibrium cell after passing through a 0.5 mm i.d. helical tube immersed in the cooling bath. The length of the tube is about 1.5 m, and at the flow rates used, thermal equilibrium is achieved.

The stirring system of the bath consists of an ac motor equipped with an impeller. Because of the small internal diameter of the glass tube, the hydrate former bubbles provide the stirring in the cell and ensure the uniform temperature distribution inside the cell.

For measuring the system pressure, two Bourdon-type pressure gauges as shown in Figure 1 are used. The first pressure gauge indicates the regulated pressure of the gas

Figure 1. Schematic of the experimental apparatus.

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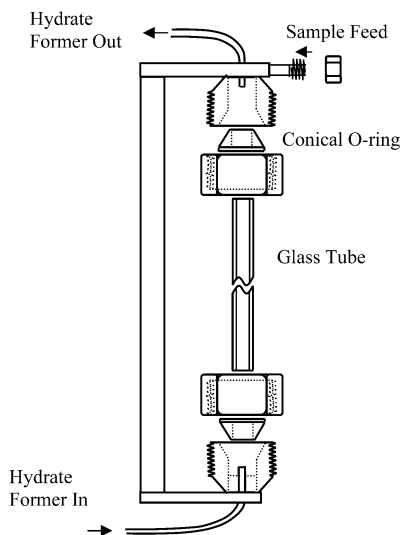
Figure 2. Cross section of the equilibrium cell.

line input to the equilibrium cell. The equilibrium glass cell pressure is measured using a Bourdon tube Heisse model-M pressure gauge from Invensys Systems Inc., Foxboro MA. The range of the pressure gauge is 0−1.378 MPa. The precision of the second pressure gauge is within ±0.007 MPa.

The temperature of the cooling bath is measured with a mercury-in-glass thermometer with a maximum error of ±0.1 K. Assuming ±0.2 K as the estimated uncertainty associated with the visual determination of dissociation conditions, the rounded down value of the total uncertainty of the measured dissociation temperature will be equal to ±0.2 K.[6] The thermometer is immersed in the bath. Its location is about 10 cm below the free surface of the bath solution in the horizontal position. Because of the low heating rate of the cooling bath during the experiment, it is assumed that this temperature is equal to the cell temperature.

Procedure. The initial temperature of the bath was lowered to the anticipated hydrate formation temperature for each experiment; consequently, the equilibrium cell was placed under a vacuum. Next, the cell was pressurized to slightly above atmospheric pressure with R22 gas; this allowed the equilibrium cell to be charged. So, after valve II was closed and valve III was opened, the aqueous solution was charged from the top of the cell as shown in Figure 2. For each experiment, approximately 40 cm³ of solution was fed. Then, valve II was opened slightly to introduce small bubbles of hydrate former into the cell. This purged the vapor phase and removed the residual air that might have entered into the equilibrium cell during the feeding of the aqueous solution. Closing valve III caused the system pressure to approach the regulated pressure. The nucleation sites did not exists at this temperature, and the bath temperature, depending on the acetone concentration, was cooled to about 8 K below the anticipated hydrate dissociation temperature. Under these conditions, the clathrates, especially at the interface of the bubbles and the water rich liquid phase, were formed. The system was kept under these conditions for about 5 h to ensure the uniform temperature distribution and steady-state condition.

After that, the cell temperature was increased at the rate of about 1 K·h⁻¹. At this stage the temperature was recorded every 0.1 K. Because of the low fluctuation of the system pressure, this parameter was also recorded at the

Table 1. Critical Properties and Acentric Factors of Acetone, Water, and R22

component	T_c/K	P_c/MPa	ω
acetone	508.2	4.700	0.318
water	647.1	22.037	0.332
R22	369.3	4.966	0.221

same interval. When the dissociation condition was reached, the hydrate crystals broke down rapidly. The temperature at which the last hydrate crystal disappeared was considered as an equilibrium hydrate dissociation temperature at the specified pressure. The crystals' dissociation was detected by the naked eye. To ensure the accuracy of the results, this procedure was repeated two or three times for each pressure. For the second and third runs, the heating rate, 1 K below the dissociation temperature obtained from the first run, was reduced to about 0.4 K·h⁻¹.

Modeling. Jager et al.[2] developed the equilibrium model based on the adsorption statistical mechanics of van der Waals and Platteeuw[5] for the system methane + water + 1,4-dioxane. Javanmardi et al.[4] extended this model to the system methane + water + acetone:

At equilibrium, the chemical potential of water in the hydrate phase is equal to the chemical potential of water in the liquid phase. Therefore, it can be shown that[7]

$$\sum_{m=1}^{2} v_m \ln(1 + \sum_{j=1}^{nc} C_{mj} f_j) =$$
$$\frac{\Delta \mu_w^\circ}{RT_0} - \int_{T_0}^{T} \frac{\Delta h_w^l}{RT^2} dT + \int_{0}^{P} \frac{\Delta v_w^l}{RT} dP - \ln a_w \quad (1)$$

where v_m is the number of cavities of type m per water molecule in the hydrate lattice, C_{mj} is the Langmuir constant for the j-th hydrate former on the type m cavity, and f_j is the fugacity of guest component j in MPa. $\Delta \mu_w^\circ$, Δh_w^l, and Δv_w^l are the differences between the chemical potentials, the enthalpies, and the specific volumes of water in the unoccupied lattice and in pure water, respectively. These parameters have been given by Holder et al.[7] T and P are the system temperature and pressure in K and MPa, respectively. Finally, a_w is the water activity and T_0 is 273.15 K.

In the model of Javanmardi et al.[4] it has been assumed that, in addition to methane, acetone molecules are entrapped in the large cavities of structure II. In other words, acetone has been considered as a water−solute hydrate former. This assumption needs suitable expressions for the acetone fugacity and Langmuir constant, as for R22. According to this model, it has been assumed that the vapor phase can be treated as a pure R22. So, the fugacity of R22 can be estimated using the Peng−Robinson equation of state[8] with the following temperature dependence of the attraction term:

$$\alpha = [1 + (0.37464 + 1.5422\omega - 0.26992\omega^2)(1 - \sqrt{T_r})]^2 \quad (2)$$

where ω is the acentric factor and T_r is the reduced temperature. The critical properties and acentric factors of acetone, water, and R22 are given in Table 1.

Moreover, the solubility of R22 in the liquid phase is insignificant. This means that the liquid phase can be considered as a binary system. On the basis of this assumption, the acetone fugacity may be calculated from the water rich liquid phase. The details of the calculations are given by Javanmardi et al.[4]

Table 2. Kihara Parameters for Acetone and R22

component	$2a$/Å	σ/Å	(ϵ/k)/K
acetone	1.936	2.835	306.66
R22	1.595	2.952	250.41

Table 3. Equilibrium Dissociation Temperatures for the System R22 (1) + Water (2) + Acetone (3)

$P_{exp}{}^a$/MPa	$T_{exp}{}^b$/K	T_{cal}/K	$(T_{exp} - T_{cal})$/K	x_3
0.154	277.8	277.1	0.7	0
0.222	280.3	279.9	0.4	
0.291	282.2	282.0	0.2	
0.326	283.2	282.8	0.4	
0.361	283.9	283.6	0.3	
0.429	285.2	285.0	0.2	
0.498	286.3	286.2	0.1	
0.567	287.2	287.2	0.0	
0.635	288.2	288.1	0.1	
0.704	288.8	288.9	−0.1	
0.773	289.4	289.6	−0.2	
0.223	279.0	279.4	−0.4	0.02
0.291	281.1	281.3	−0.2	
0.360	282.7	282.9	−0.2	
0.429	284.2	284.2	0.0	
0.498	285.4	285.3	0.1	
0.567	286.4	286.3	0.1	
0.636	287.4	287.2	0.2	
0.704	287.9	288.0	−0.1	
0.223	278.2	278.7	−0.5	0.04
0.292	280.2	280.6	−0.4	
0.362	281.9	282.1	−0.2	
0.429	283.4	283.4	0.0	
0.498	284.7	284.5	0.2	
0.567	285.7	285.4	0.3	
0.223	277.3	277.9	−0.6	0.06
0.292	279.7	279.8	−0.1	
0.360	281.4	281.3	0.1	

^{a} Pressure uncertainty: ±0.007 MPa. ^{b} Temperature uncertainty: ±0.2 K.

The Langmuir constant describes the hydrate former–water interaction in the hydrate phase and depends on temperature. Most commonly, the Kihara potential with a spherical core is used for describing the guest molecule and one water molecule interaction.[9]

The Kihara parameters of acetone have been given by Javanmardi et al.[4] These parameters are optimized by minimizing the difference between the calculated and experimental equilibrium temperatures of methane hydrate in the presence of water + acetone given by Mainusch et al.[1] For R22, the core radius, a, is estimated from the correlation presented by Tee et al.[10] The distance parameter, σ, and characteristic energy, ϵ, are optimized by minimizing the difference between the calculated and experimental equilibrium temperatures of R22 hydrate in the presence of pure water, given by Chun et al.[11] The Kihara parameters of acetone and R22 are given in Table 2.

Results and Discussions

The experimentally determined hydrate dissociation conditions as a function of acetone concentrations, the model predictions,[4] and the temperature errors have been given in Table 3.

To verify the experimental apparatus as well as the procedure, the dissociation temperatures of the R22 + water system measured in this work have been compared with the reported values,[11] as shown in Figure 3. The predicted hydrate dissociation conditions based on the model of Holder et al.[7] have also been included in this figure. It should be noted that the Kihara parameters of R22 are optimized using the experimental data of Chun et al.[11]
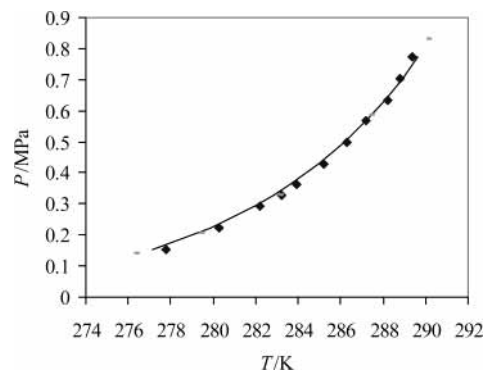

Figure 3. Hydrate dissociation conditions for the water + R22 system: shaded dashes, Chun et al.;[11] ◆, this work; solid line, the model prediction.

Table 4. Average Absolute Error of the Hydrate Dissociation Temperatures for the System R-22 (1) + Water (2) + Acetone (3)

no. of data points	pressure range/ MPa	x_3	AAE^a/K
11	0.154−0.773	0.00	0.3
8	0.223−0.704	0.02	0.2
6	0.223−0.567	0.04	0.3
3	0.223−0.360	0.06	0.3

^{a} AAE $= (1/n)\sum_{i=1}^{n}|(T_{exp} - T_{cal})|_i.$

Table 5. Promoting Effect of Acetone on the Dissociation Temperatures for the System R22 (1) + Water (2) + Acetone (3)

P_{exp}/MPa	T_{exp}/K	$T_{cal}{}^a$/K	$T_{cal}{}^b$/K	x_3
0.223	279.0	279.4	278.5	0.02
0.291	281.1	281.3	280.6	
0.360	282.7	282.9	282.3	
0.429	284.2	284.2	283.7	
0.498	285.4	285.3	284.9	
0.567	286.4	286.3	285.9	
0.636	287.4	287.2	286.8	
0.704	287.9	288.0	287.6	
0.223	278.2	278.7	277.3	0.04
0.292	280.2	280.6	279.4	
0.362	281.9	282.1	281.1	
0.429	283.4	283.4	282.5	
0.498	284.7	284.5	283.6	
0.567	285.7	285.4	284.7	
0.223	277.3	277.9	276.2	0.06
0.292	279.7	279.8	278.3	
0.360	281.4	281.3	279.9	

^{a} Acetone as a hydrate former. ^{b} Acetone as a nonhydrate former.

The equilibrium conditions for the system R22 + water + acetone have been given in Figures 4 for 0.02, 0.04, and 0.06 mole fraction of acetone. Also, the predicted values of the model developed by Javanmardi et al.[4] have been included in these figures.

The average absolute errors of the dissociation temperatures for the system R22 + water + acetone have been given in Table 4. As shown in this table, the measured values are in good agreement with the predicted values. The overall pattern for different concentrations of acetone is similar.

The model predictions and the calculated dissociation temperatures based on the assumption of acetone as a nonhydrate former have been given in Table 5. The results for the case of acetone as a nonhydrate former indicate the inhibition effect of acetone due to the water activity reduction. As shown in this table, acetone is a hydrate forming compound, but its hydrate forming characteristics are in competition with its hydrate inhibition effect.
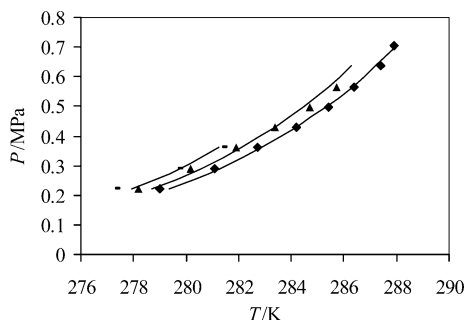
Figure 4. Hydrate dissociation conditions for the water (1) + R22 (2) + acetone (3) system: ◆, $x_3 = 0.02$; ▲, $x_3 = 0.04$; dashes, $x_3 = 0.06$; solid lines, the model prediction.

As shown in Figures 3 and 4 and Table 3, acetone has an inhibition effect for all of the investigated acetone concentrations. This is in contrast to the behavior of the methane + water + acetone system.[1,3,4]

The results show that the inhibition or promotion effect of acetone depends on the vapor phase hydrate former as well as the water-solute hydrate former concentration.

Conclusion

Acetone had an inhibition effect on R22 hydrate dissociation conditions for mole fractions of acetone equal to 0.02, 0.04, and 0.06. The equilibrium conditions were measured in the pressure range 0.223 to 0.704 MPa.

The previous model for methane hydrate in the presence of acetone + water was applied to predict the equilibrium conditions for this system. The measured values were in good agreement with the predicted values.

Acetone is a hydrate forming compound. At high concentrations of acetone, its hydrate inhibition effect due to the water activity reduction is higher than its promoting effect.

Interest in the promotion effect of water-solute hydrate formers was increased when it was suggested that these compounds could be used to store natural gas in stabilized gas hydrates at higher temperatures. This work showed that the inhibition or promotion effect of acetone as a water-solute hydrate former depended on its concentration as well as the vapor phase hydrate former.

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