

The Occurrence of Methane Hydrate in Ternary and Quaternary Systems of Methane, Water, Certain Organics, and Sodium Chloride

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ABSTRACT: From literature it is known that sodium chloride (NaCl) exerts a strong pressure enhancing effect on the three-phase equilibrium liquid water-hydrate-vapor (L_w -H-V) in the ternary system water + methane + sodium chloride ($H_2O + CH_4 + NaCl$). However, on the other hand, it recently became apparent that certain water-soluble organic components, present in low concentrations in the aqueous phase, exert the opposite effect on the equilibrium pressure of the three-phase equilibrium L_w -H-V. Compared to the hydrate equilibrium pressure of the organic free liquid phase, pressure reductions as high as 80% have been observed. This paper reports on experimental results of the competitive effect on the equilibrium pressure of the three-phase equilibrium L_w -H-V, of both NaCl and the water-soluble organic component 1,3-dioxolane. We also consider the effect on the hydrate equilibrium pressure of organic components that are very poorly soluble in water, for example, tetrahydropyran, cyclobutanone, methylcyclohexane, fluoroform (CHF_3), and tetrafluoromethane (CF_4). These poorly water-soluble components are referred to as water-insoluble.

INTRODUCTION

A few decades ago industry initiated an investigation of the possibility for storing natural gas as gas hydrates in salt caverns. Knowledge about the influence of sodium chloride (NaCl), present at saturation conditions, on the three-phase equilibrium liquid water-hydrate-vapor (L_w -H-V) was of crucial importance. The research executed at that time showed that NaCl exerts a strong hydrate inhibiting effect, resulting in a significant increase of the pressure of the three-phase equilibrium L_w -H-V. For instance, the hydrate equilibrium pressures may increase from 10 MPa in the absence of NaCl to values as high as 80 MPa in the presence of certain concentrations of NaCl, depending, of course, on temperature. A practical consequence of this finding was that storage of natural gas in salt caverns was not considered to be an attractive option.¹

Recently it was discovered²⁻⁵ that low concentrations of certain organic components (e.g., acetone, 1,4-dioxane, and tetrahydrofuran) show the opposite effect—

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these components show a hydrate promoting effect. The promoting effect frequently results in a significantly reduced hydrate equilibrium pressure when compared to the pressure of L_w-H-V for the system $H_2O + CH_4$. From the experimental results it was concluded that the maximum pressure reduction occurred at organic component concentrations of approximately 6 mole%, relative to water. However, at higher organic concentrations in the aqueous solution, a steady increase in hydrate equilibrium pressure was observed, that is, less reduction and eventually inhibition of the hydrate equilibrium occurs. In this respect the behavior of water-soluble additives differs from the influence of NaCl on the hydrate equilibrium pressure. The latter exhibits a continual pressure increase with increasing concentration.

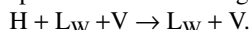
Use of gas hydrates for storage and transportation of natural gas has not yet been put into practice, because hydrate equilibrium pressures were too high. The presence of specific organic components seems to be able to reduce these pressures and might enable gas hydrates to offer a practical option. Examples of practical cases in which salts and hydrate formers may be present are storage of natural gas in emptied salt caverns and decomposition of deposits of natural gas hydrates by hot brine injection. It can be advantageous to store natural gas in the form of hydrates to improve the load factor of natural gas supply systems. Benesh⁷ already mentioned this idea in 1942. Under standard conditions hydrates occupy 150 to 170 times less volume than the corresponding highly compressed gas.⁸ If an appropriate equilibrium pressure-reducing additive for natural gas hydrate can be found it would, in principle, be possible to store natural gas at ambient temperatures and low pressures, in contrast to the conditions required for liquefying natural gas.

All of those new developments in gas hydrate research require a good insight into the phase behavior of different kinds of hydrate systems, with or without NaCl or other salts. The main purpose is to find organic components that reduce the hydrate equilibrium pressure, acting as promoters, and to investigate the competing effects they exhibit with the hydrate inhibiting effect of NaCl. The organic components chosen for this paper were 1,3-dioxolane, which is soluble in water, and tetrahydropyran, cyclobutanone, and methylcyclohexane, which are very poorly soluble in water (referred to as insoluble). We also studied the influence of fluoroform (CHF_3) and tetrafluoromethane (CF_4), which are insoluble in water when liquefied, but are soluble in the gaseous state under the conditions used here. Only for the water-soluble organic 1,3-dioxolane has the competing effect with NaCl been studied at present and this is presented in this paper.

EXPERIMENTAL

The experiments were carried out in a so-called Cailletet apparatus. In this apparatus phase equilibria for mixtures of known overall composition can be determined visually to pressures as high as 15 MPa. For details of this experimental equipment, see References 9 and 10. Temperatures were determined to an accuracy better than 0.05 K and the pressures were measured to an accuracy better than 0.005 MPa. The different types of systems, with water-soluble and water-insoluble additives, require different measuring regimes and are described below:

1. *Systems with $H_2O + CH_4$ + water-soluble additive.* These systems show three phases when hydrates are present, which means that there are two degrees of freedom in a system with three components. In the pT -diagram the conditions are described in terms of a region that consists of different pT -curves for different compositions of the system. To describe the hydrate equilibrium the temperature of hydrate disappearance is determined at a preset pressure and for several concentrations of the additive. The line for hydrate disappearance is considered to be the hydrate equilibrium line and represents the following phase transition:



The pressure is preset, using a dead-weight pressure balance, and the sample is then cooled below the equilibrium temperature. When the hydrate phase precipitates, the temperature is increased gradually until the last hydrate crystal disappears. This temperature is considered to be the equilibrium temperature for the preset pressure value. The system of this type we considered is $H_2O + CH_4 + 1,3$ -dioxolane.

2. *Systems with $H_2O + CH_4$ + water-soluble additive + NaCl.* When hydrates are present, this system has three degrees of freedom. These are only three phases, because both the additive and the NaCl are dissolved in the water phase. This means that the hydrate equilibrium pressure depends on temperature and on the concentrations of additive and NaCl. The same transition of phases is determined as above—that is, the hydrate disappearance line—and the same measuring regime is followed. The system of this type that was considered is $H_2O + CH_4 + 1,3$ -dioxolane + NaCl.

3. *Systems with $H_2O + CH_4$ + water-insoluble additive.* When hydrates are present, four clearly distinct phases are present, which means that this system has only one degree of freedom. Therefore, when the temperature is set, the pressure will adjust itself and the univariant equilibrium conditions can be measured directly. The water-insoluble additives that were investigated in the presence of water and methane were: tetrahydropyran, cyclobutanone, methylcyclohexane, CHF_3 , and CF_4 .

When the conditions for hydrate disappearance are measured, it is assumed that at the temperature at which the hydrate phase is about to disappear, all methane is present only in the vapor phase. Furthermore, it is assumed that this phase consists of pure methane. Under these assumptions, the compositions of the fluid phases for

TABLE 1. Purity of the chemicals used

| Chemical | Supplier | Purity (mole%) |
|--------------------|------------------|----------------|
| water | — | Distilled |
| methane | Air Products | 99.99 |
| NaCl | Baker | 99.6 |
| 1,3-dioxolane | MERCK-Schuchardt | > 99 |
| tetrahydropyran | Acros | > 99 |
| cyclobutanone | MERCK-Schuchardt | 99.5 |
| methylcyclohexane | MERCK-Schuchardt | > 99 |
| fluoroform | Air Products | 99.5 |
| tetrafluoromethane | Air Products | 99.5 |

both the ternary and quaternary systems are known and, as a good approximation, the three-phase L_w -H-V equilibrium behaves as a univariant system. The purity of the chemicals used to prepare the samples is summarized in TABLE 1.

EXPERIMENTAL RESULTS

Experimental results for the various types of systems with the additives used are discussed in this section. The pT -equilibrium lines for the systems with water-soluble additives seem quite complicated, showing a dependence on the concentration of additive. For these systems the pressure values are normalized or even double-normalized to elucidate the simultaneous influence of the additive and NaCl on the methane hydrate equilibrium and the influence of the additive alone, respectively. The relations that are used to normalize or double-normalize the pressure data are:

$$P_{\text{normalized}} = \frac{P_{\text{experimental}}}{P_{\text{water + methane}}}, \quad P_{\text{double-normalized}} = \frac{P_{\text{experimental}}}{P_{\text{water + methane + NaCl}}}.$$

Normalization and double-normalization is normally applied to the px -curves at various temperatures. Normalization of pressure follows from division of the experimental pressure of the ternary or quaternary system by the equilibrium pressure of the system $H_2O + CH_4$ at that particular temperature. The results of this operation are given in the FIGURES 2A–5A. Double-normalization of pressure follows from division of the experimental pressure of the quaternary system by the equilibrium pressure of the system $H_2O + CH_4 + NaCl$ at that particular temperature. Results of this operation are given in the FIGURES 2B–5B. The normalized curves can cross the value one, in particular in the systems with NaCl, which means that the hydrate equilibrium is inhibited rather than promoted.

The system $H_2O + CH_4 + 1,3$ -dioxolane has been investigated by de Deugd.¹¹ The presence of additive shows a significant hydrate pressure reduction up to 1,3-dioxolane concentrations of about 5–6 mole% in the water phase. At higher concentrations the pressure reduction again decreases. The highest pressure reduction retrieved is approximately 80% compared to the hydrate equilibrium pressures of the organic-free system ($H_2O + CH_4$). The reduction in hydrate equilibrium pressure was promising enough to study the influence of 1,3-dioxolane in the presence of NaCl. Experimental data were collected by Reuvers for the system containing $H_2O + CH_4 + 1,3$ -dioxolane + NaCl, with several concentrations of NaCl in the liquid water phase up to saturation—approximately 8 mole%. For each concentration of NaCl several concentrations of 1,3-dioxolane dissolved in the water phase were examined.

FIGURE 1 represents the primary experimental results of the quaternary system with 2 mole% NaCl and various concentrations of 1,3-dioxolane in a pT -diagram. In FIGURE 2 the normalized and double-normalized px -diagrams of the data are shown, in which the simultaneous influence of 1,3-dioxolane and NaCl and of 1,3-dioxolane alone can be observed. FIGURES 3 to 5 show the normalized and double-normalized hydrate equilibrium pressures for higher concentrations of NaCl. The figures show clearly that at concentrations lower than approximately 6 mole% the equilibrium pressure decreases with increasing mole fraction of 1,3-dioxolane present in the water phase. When the concentration of 1,3-dioxolane is further

increased, the pressure-reducing effect decreases again. This value for the concentration of the organic at maximum hydrate equilibrium pressure reduction was also observed with other water-soluble additives. The same trend is seen in the presence of NaCl. That is, the minimum in the curves (indicating the highest reduction) is located between 5 and 6 mole% of 1,3-dioxolane, although the present concentration of NaCl varies. In the normalized diagrams of FIGURES 2A–5A it can be observed that the promoting effect of 1,3-dioxolane is able to compete with the inhibiting effect of NaCl up to a concentration of 6 mole% NaCl, which is just below saturation. At higher NaCl concentrations, the 1,3-dioxolane still reduces the hydrate equilibrium but not to such an extent that the hydrate equilibrium pressure is lower than the equilibrium pressure of the system $\text{H}_2\text{O} + \text{CH}_4$. The diagrams with the double-normalized pressure show that the influence of 1,3-dioxolane is the same for varying concentrations of NaCl. Thus, synergistic and antagonistic effects of the additive component and NaCl cannot be observed. In FIGURE 6 the influence of NaCl can be seen in a px -diagram, where the pressure dependency on the mole fraction of NaCl is given for several temperatures at a mole fraction of 1,3-dioxolane of 0.05.

For systems with an additive that is insoluble in water, the dependency on concentration of the additive is not important to the phase equilibrium. The phase equilibrium is represented by an univariant line and can be measured directly. Therefore, normalization or double-normalization of the pressures is not really required to obtain a clear insight into the influence of the additives. The hydrate equilibrium lines of the three additives that are in the liquid state, over the pressure and temperature range considered, are shown in FIGURE 7. This is a pT -diagram and the solid line gives the line of the methane hydrate equilibrium. It can be clearly observed that

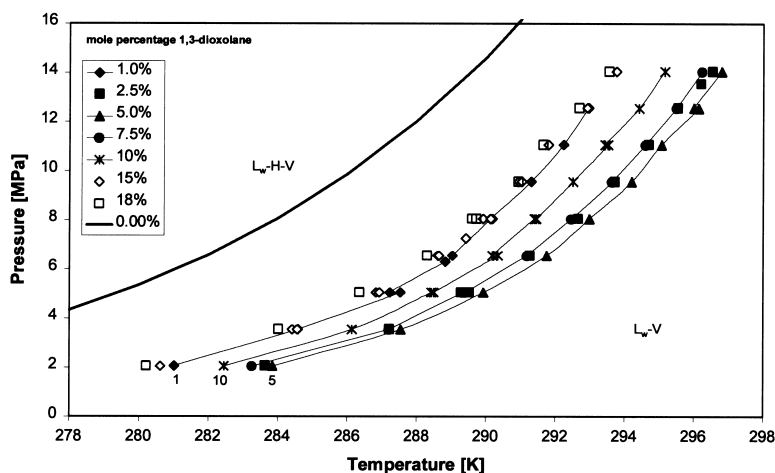


FIGURE 1. pT -diagram of the system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The concentration of NaCl is 2 mole% and the pT -curves are given for various concentrations of 1,3-dioxolane; 1 mole% (\blacklozenge), 2.5 mole% (\blacksquare), 5 mole% (\blacktriangle), 7.5 mole% (\bullet), 10 mole% ($*$), 15 mole% (\diamond), and 18 mole% (\square). The solid line is the hydrate equilibrium curve of the system $\text{H}_2\text{O} + \text{CH}_4$.

the pressure reduction by tetrahydropyran and cyclobutanone is significant, namely greater than 70%. The promoting effect of methylcyclohexane is considerably smaller, approximately 25%. It should be noted that this last component is expected to form sH hydrate,¹² in contrast to the presence of the other two additives, which are believed to form sII. For gas storage and transportation purposes sH might be a more attractive structure because of the larger potential storage capacity¹³ and a reduction of 25% in the hydrate equilibrium pressure is still considerable.

The other two additives that are insoluble in water were CHF₃ and CF₄. These fluoroalkanes were chosen because of their known formation of gas hydrates in systems with water. Both components are in the vapor phase over the pressure and

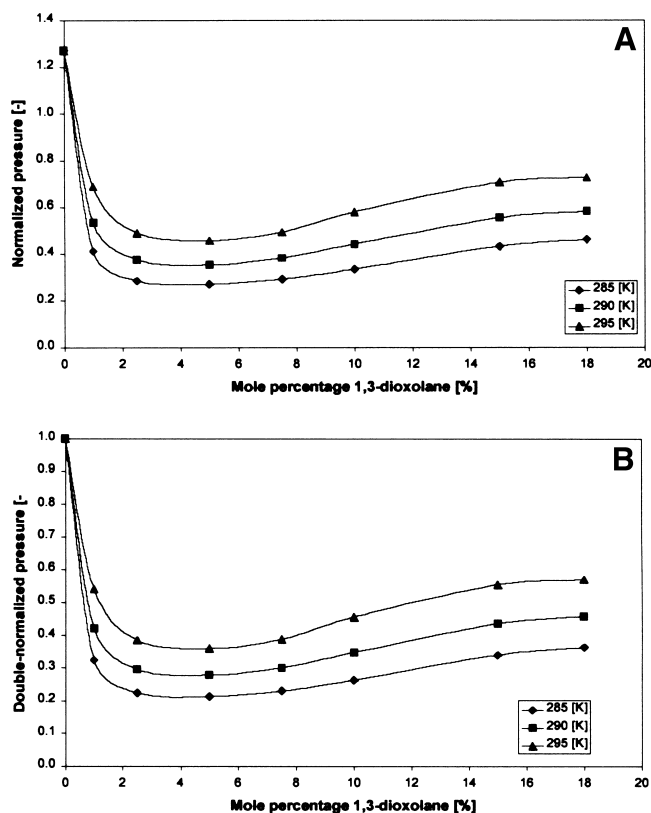


FIGURE 2. A. Normalized px -diagram of the system with H₂O + CH₄ + 1,3-dioxolane + NaCl. The normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 2 mole%. B. Double-normalized px -diagram of system with H₂O + CH₄ + 1,3-dioxolane + NaCl. The double-normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 2 mole%.

temperature range considered; in fact, CF_4 is in a supercritical state. The CHF_3 flashed in the temperature range studied; although it is insoluble in water no clear distinct fourth phase (liquid additive phase) could be observed. Therefore, hydrate disappearance conditions were measured at various compositions of the vapor phase, 0.25, 0.50 and 0.75 mole fraction of CHF_3 . The hydrate equilibrium of the system $\text{H}_2\text{O} + \text{CHF}_3$ was also measured. This was also previously determined by Kubota *et al.*¹⁴ Both data sets showed similar results with hydrate equilibrium pressures that were lower than those for the system $\text{H}_2\text{O} + \text{CH}_4$. The systems with the mixtures of CH_4 and CHF_3 showed hydrate equilibrium pressures between those for the systems $\text{H}_2\text{O} + \text{CHF}_3$ and $\text{H}_2\text{O} + \text{CH}_4$. All these lines are shown in FIGURE 8. The mixture

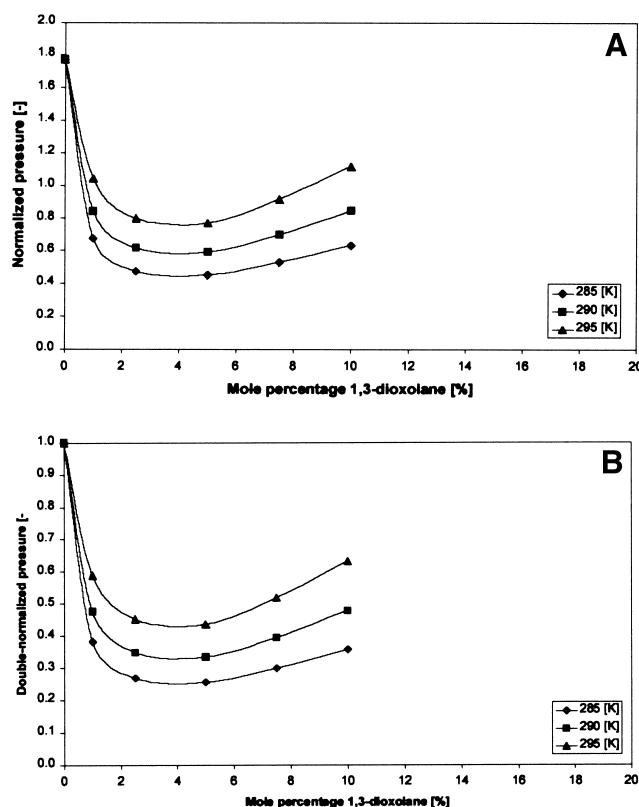


FIGURE 3. A. Normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (\blacklozenge), 290 K (\blacksquare), and 295 K (\blacktriangle). The content of NaCl is 4 mole%. B. Double-normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The double-normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (\blacklozenge), 290 K (\blacksquare), and 295 K (\blacktriangle). The content of NaCl is 4 mole%.

with the relative small fraction of CHF_3 (circles in the figure)—an attractive feature for technological applications of gas hydrates with natural gas—shows reductions of nearly 60%.

The supercriticality of CF_4 makes it impossible to observe a fourth distinct phase and, therefore, the same experimental regime as for CHF_3 was followed. All the hydrate equilibrium pressures are compared to the equilibrium of the system $\text{H}_2\text{O} + \text{CH}_4$, and also to the measurements performed on the system $\text{H}_2\text{O} + \text{CF}_4$. The hydrate equilibrium pressures for the system $\text{H}_2\text{O} + \text{CF}_4$ show higher values than those for

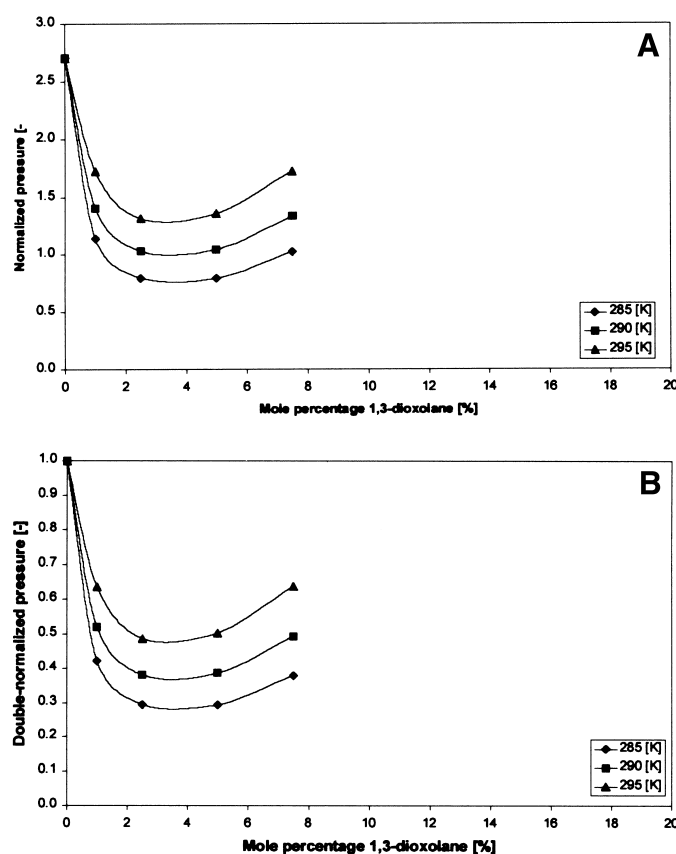


FIGURE 4. A. Normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 6 mole%. B. Double-normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The double-normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 6 mole%.

the system $\text{H}_2\text{O} + \text{CH}_4$. Therefore, CF_4 can be assumed to be an inhibitor or very weak promoter. The systems with mixtures of CH_4 and CF_4 in the vapor phase that were considered had compositions of 0.25, 0.5, and 0.75 mole fraction of CF_4 . The mixture with the smallest fraction of CF_4 shows reduction of the methane hydrate equilibrium pressure slightly larger than 20%. The equimolar mixture of CH_4 and CF_4 shows less reduction and the mixture with 0.75 mole fraction CF_4 shows elevation of the methane hydrate equilibrium pressure. This information is summarized in FIGURE 9.

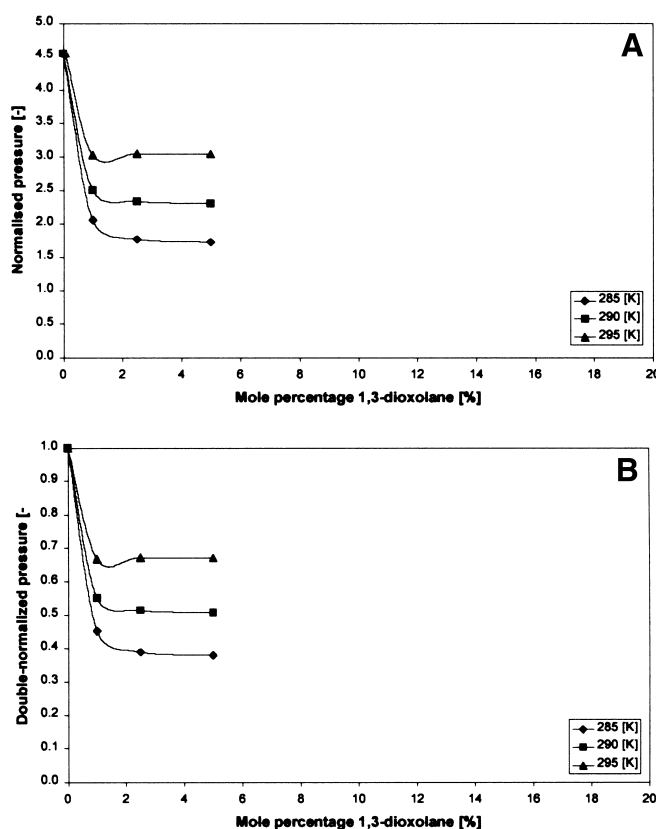


FIGURE 5. A. Normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 8 mole%. B. Double-normalized px -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The double-normalized pressure is given as a function of the mole fraction 1,3-dioxolane at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲). The content of NaCl is 8 mole%.

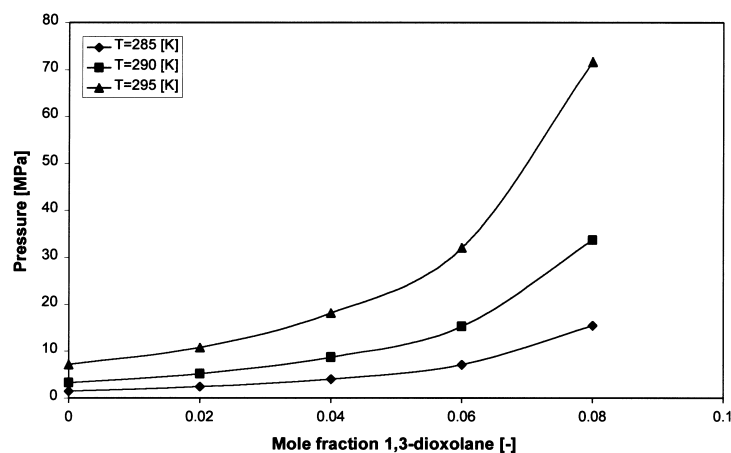


FIGURE 6. p - x -diagram of system with $\text{H}_2\text{O} + \text{CH}_4 + 1,3\text{-dioxolane} + \text{NaCl}$. The pressure is given as a function of the mole fraction NaCl at various temperatures; 285 K (◆), 290 K (■), and 295 K (▲), and a content for 1,3-dioxolane of 5 mole%.

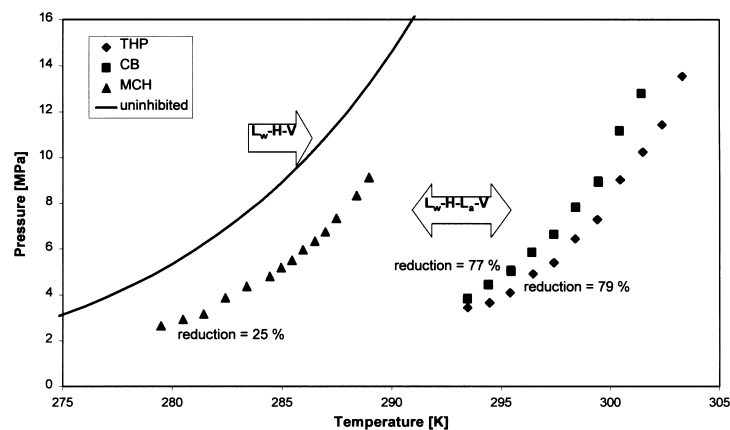


FIGURE 7. p - T -diagram of systems with $\text{H}_2\text{O} + \text{CH}_4 + \text{additive}$ with the four-phase hydrate equilibrium given for the additives: tetrahydropyran (◆), cyclobutanone (■), and methylcyclohexane (▲). The hydrate equilibria are compared to the hydrate equilibrium of the system $\text{H}_2\text{O} + \text{CH}_4$ (solid line).

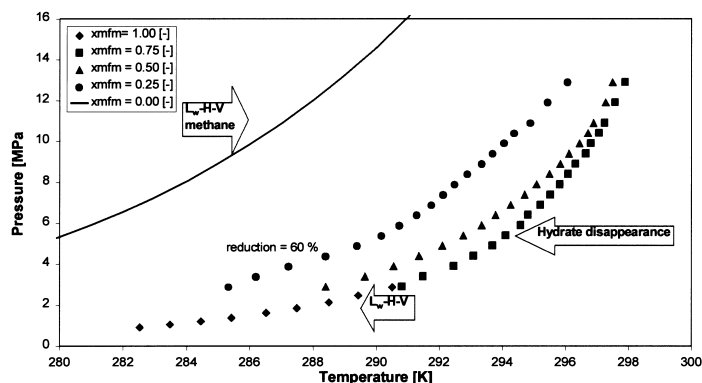


FIGURE 8. pT -diagram of systems with $\text{H}_2\text{O} + \text{CH}_4 + \text{CHF}_3$ with the hydrate equilibrium pressures for various mole fractions of CHF_3 in the vapor phase: 1.00 (\blacklozenge), 0.75 (\blacksquare), 0.50 (\blacktriangle), and 0.25 (\bullet). The hydrate equilibria are compared to the hydrate equilibrium of the system $\text{H}_2\text{O} + \text{CH}_4$ (solid line).

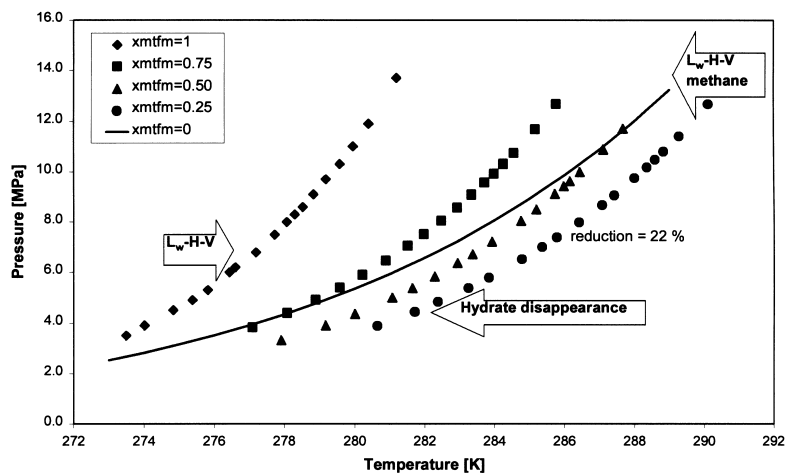


FIGURE 9. pT -diagram of systems with $\text{H}_2\text{O} + \text{CH}_4 + \text{CF}_4$ with the hydrate equilibrium pressures for various mole fractions of CF_4 in the vapor phase: 1.00 (\blacklozenge), 0.75 (\blacksquare), 0.50 (\blacktriangle), and 0.25 (\bullet). The hydrate equilibria are compared to the hydrate equilibrium of the system $\text{H}_2\text{O} + \text{CH}_4$ (solid line).

DISCUSSION AND CONCLUSIONS

L_w-H-V equilibrium lines for the systems H₂O + CH₄ + 1,3-dioxolane and H₂O + CH₄ + 1,3-dioxolane + NaCl have been measured. The measurements were carried out for sodium chloride concentrations of 2, 4, 6, and 8 mole% and at 1,3-dioxolane mole fractions ranging from 0.01 to 0.18. The operational pressure of the Cailletet equipment ranged from 2 to 14 MPa. Equilibrium temperatures at these pressures ranged from 270 K to 297 K. From the experimental results it was concluded that the organic compound 1,3-dioxolane, which is soluble in water, shows a hydrate promoting effect at low concentrations. In all cases, the lowest equilibrium pressure was measured at a 1,3-dioxolane concentration of approximately 6 mole%. Adding NaCl to the system increases the equilibrium pressure significantly, though the competing effect of 1,3-dioxolane is large enough to overrule this effect up to NaCl concentrations of 6 mole%. The minimum hydrate equilibrium pressure at 6 mole% of additive might be due to the formation of sII hydrate.¹¹ The value of approximately 5 mole% complies with the concentration of large cavities relative to the water molecules. Confirmation of this result should be obtained, for example, by using spectroscopic methods.

The comparable competing effect between NaCl and water-insoluble additives as obtained with the water-soluble additives remains to be investigated. However, thus far the promoting effects of the water-insoluble additives tetrahydropyran, cyclobutanone, methylcyclohexane, and CHF₃ on the methane hydrate equilibrium show promising results and justify further study for practical applications that require hydrate equilibrium pressure reduction. If the hydrate pressure reducing capacities of the water-insoluble additives are comparable to those of the water-soluble ones, then they have one significant advantage for practical application. Their insolubility in water could reduce the number of separation steps in processes that use application of gas hydrate technology. The behavior of CHF₃ and CF₄, which have a molecular structure similar to CH₄, seems comparable to that of CH₄ and thus study of the hydrate aspects of this type of component might be of importance for a fundamental understanding of gas hydrate formation and their stability.

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