Hydrate Inhibition with Methanol – A Review and New Concerns over Experimental Data Presentation

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Abstract

Hydrate inhibition with methanol continues to play a critical role in many operations. Opportunities exist at many facilities for optimizing the amount of methanol required based on the operating conditions. To properly predict these requirements, the distribution of the methanol between the gas and liquid phases is of key importance. Significant contributions by the GPA research program both in past years and current or future research projects make it possible to better predict methanol requirements for hydrate inhibition from commercial simulators. However, a proper understanding of experimental methods and actual sample and overall compositions is very important to an accurate interpretation of the results.

Introduction

As defined by the Gas Processors Engineering Data Book [1], a hydrate is a physical combination of water and other small molecules to produce a solid which has an "ice-like" appearance but possesses a different structure than ice. It is generally recognized that two common forms of hydrates exist in the gas processing industry, each having its own crystalline structure. Structure I is formed by water and smaller molecules such as methane, ethane, carbon dioxide and hydrogen sulfide while Structure II is formed by larger molecules such as propane and isobutane. In each case, the water molecules form the crystalline structure or lattice and the hydrate formers occupy the cavity of that lattice. In more recent years, efforts have been taken to also predict the formation of a third type of hydrate, Structure H involving large molecules.

In situations where hydrates are likely to form, several methods are available to prevent or suppress their occurrence. In some cases, simple manipulation of the system temperature and pressure may be adequate to eliminate hydrates. Water removal or dehydration of the process stream via regenerated glycol systems or molecular sieves is very effective. However, in some cases it may not be cost effective to implement one of these methods. For those areas, the injection of either ethylene glycol (EG) or methanol is typically the favorite of choice due to their inherent properties of hydrate suppression. Gathering or pipeline systems and gas processing facilities are common places to find hydrate suppression systems. The presence of water in produced gas can easily lead to hydrate formation in the pipeline as the temperature decreases or pressure increases. In addition, hydrate suppression is commonly used in refrigeration plants or natural gas liquids extraction facilities.

Relative to hydrate suppression, methanol has several properties which make it especially well suited for the application when compared to other solvents. Methanol exhibits a lower viscosity and surface tension as a function of temperature. The most noted drawback of methanol is its high vapor pressure which is significantly higher than that of the traditional glycols resulting in potentially high losses at certain conditions. In addition to hydrate suppression, methanol has other uses and benefits in the gas processing industry. Methanol has been used successfully in acid gas removal, hydrocarbon dew point control and dehydration.
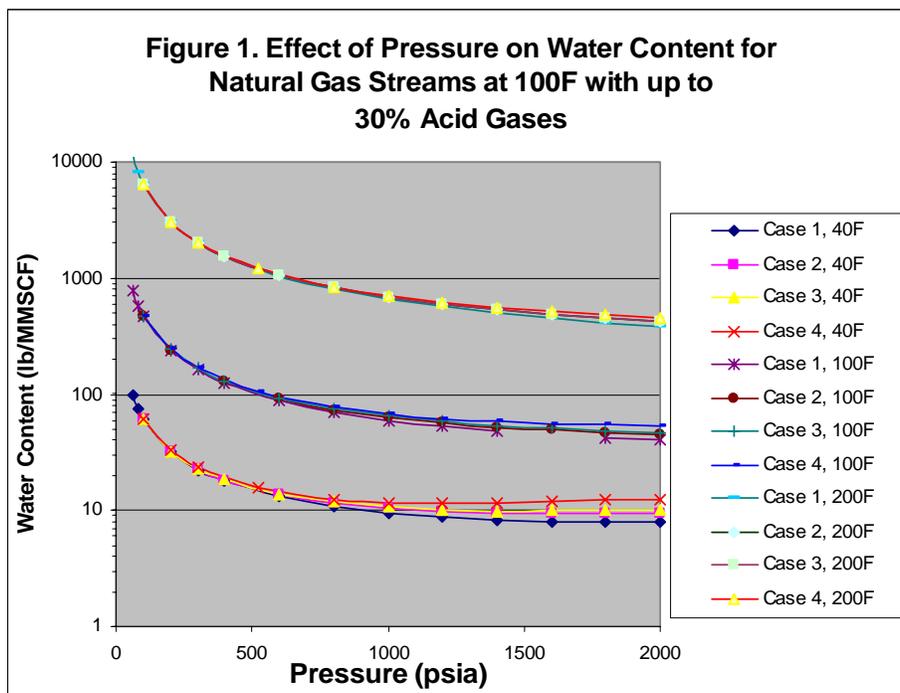
Water Content

When determining the conditions necessary for hydrate formation, it is important to understand the competing factors involved. Composition, temperature and pressure all play roles in determining whether a hydrate will form. Obviously, water and hydrate formers must be present, but the relative concentration of each can play a significant role.

It is known that H_2S and CO_2 can greatly impact the water content of a gas at certain conditions such as high pressure or at very high concentrations such as the amine regenerator off gas. However, the impact of these components on the water content of mostly hydrocarbon streams is much less. GPSA describes these effects and provides several graphical representations for certain mixtures of hydrocarbons and acid gas and the effect of temperature on water content for a given pressure. When evaluating the effect of pressure on a system with acid gas present, most data

are reported for acid gas compositions above 70 %. Little information is provided on the pressure effect for gas streams with acid gas compositions of less than 20 %. Calculations for pressure dependency on varying amounts of acid gases were performed using the process simulator ProMax® [2]. The compositions are shown in Table 1 with the resulting curves in Figure 1. The water content was based on saturation at 100°F. As shown, pressure does not have a significant impact on the systems chosen until the pressure reaches approximately 700 psia. This is in agreement with methods presented in the GPSA data book that state corrections should be made to gas mixtures containing more than 5 % H_2S and/or CO_2 at pressures greater than 700 psia. Our predictions, as shown in Figure 1, indicate that departures from this behavior increase as temperature decreases and pressure increases. Also, this behavior is proportional to the amount of acid gas.
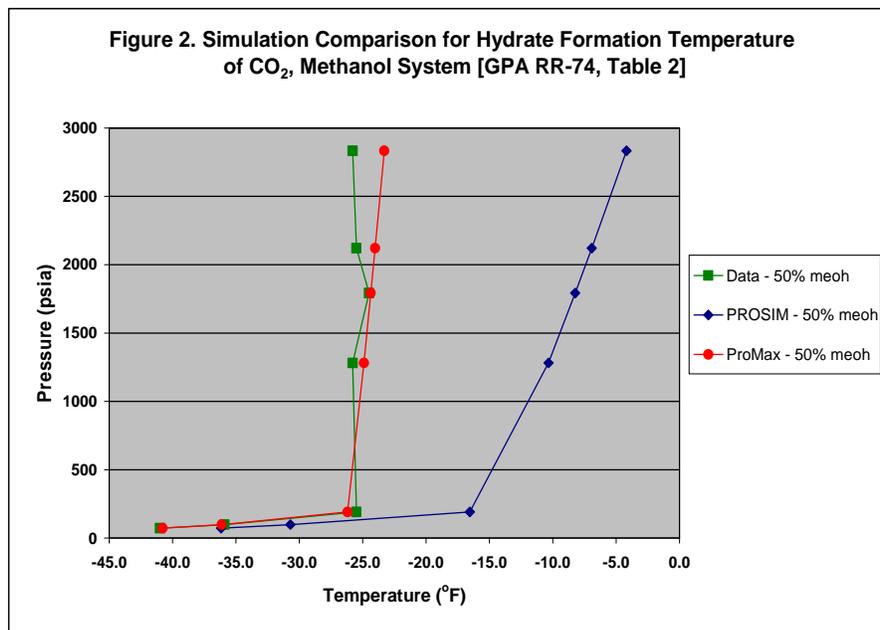
Table 1. Gas Composition used in Figure 1

Composition (Mole%)				
	Case 1	**Case 2**	**Case 3**	**Case 4**
Methane	88	74.9	73	61.6
Ethane	6	5.1	5	4.2
Propane	3	2.5	2.5	2.1
Butane	1.5	1.2	1.2	1.05
Hexane	1	0.8	0.8	0.7
Heptane	0.5	0.5	0.5	0.35
CO2	**0**	**5**	**15**	**15**
H2S	**0**	**10**	**2**	**15**

Figure 1. Effect of Pressure on Water Content for Natural Gas Streams at 100F with up to 30% Acid Gases
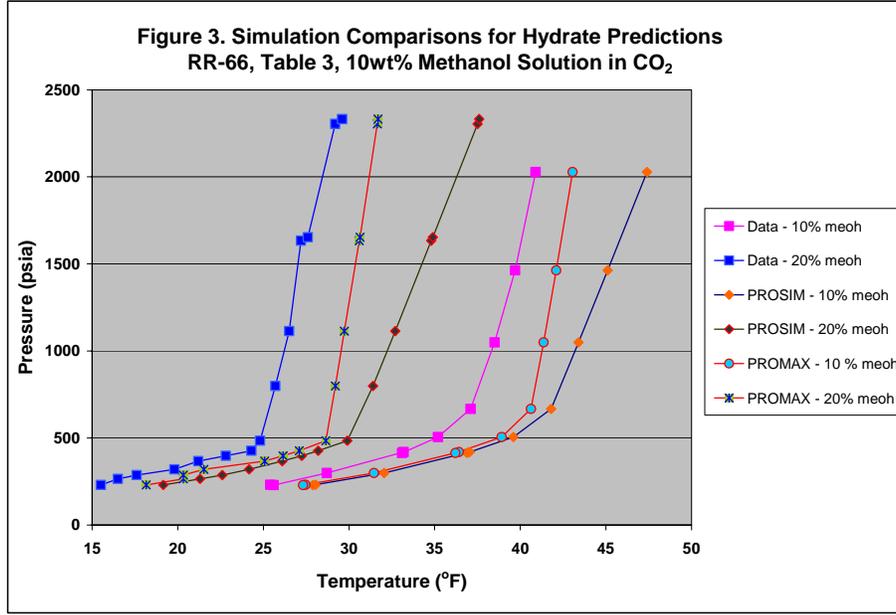
Hydrate Predictions

Hydrate formation pressure and temperature conditions are presented in several literature sources including GPA research reports RR-66 (Ng and Robinson (1983)) [3], RR-74 (Ng and Robinson (1984)) [4], RR-87 (Ng et al. (1985a)) [5], RR-92 (Ng et al. (1985b)) [6], and RR-106 (Ng et al. (1987)) [7]. For measurements involving methanol inhibition, the reported values include the pressure, temperature, and the concentration of methanol in water solution mixed with the hydrate former. However, no mention of the overall composition or the ratio of hydrate former to inhibitor solution for the hydrate measurements is provided in any of these reports. In some of the reports, the overall composition may be approximately inferred by phase equilibrium data presented, but these data do not extend to the higher inhibitor concentrations presented, the region where they are most needed. This makes predictions of hydrate formation conditions in process simulators difficult to verify in cases where the mutual solubility of the hydrate former and inhibitor is relatively high. Without knowledge of the overall composition, a significantly wide range of predicted conditions is possible. More significantly, depending on the nature of the system, caution must be exercised when using these experimental data for design or other use since the reported conditions are for an unknown overall composition.

This discussion evolved from an observation during the testing period of ProMax, particularly with regard to predicting water content and hydrate forming conditions. The hydrate formation temperature predicted by ProMax in some cases was quite different than PROSIM®. It was known that differences would exist between the two programs, and expectations were that ProMax would be superior to matching experimental data compared to PROSIM, primarily due to the ability of ProMax to better predict the phase equilibrium data for some systems. The result may be seen in Figure 2 and Figure 3. However, it was unexpected that the predictions from both simulators were quite sensitive to the overall composition for some systems, especially in liquid-liquid regions, as explained below.

Figure 2. Simulation Comparison for Hydrate Formation Temperature of CO_2, Methanol System [GPA RR-74, Table 2]

Figure 3. Simulation Comparisons for Hydrate Predictions
RR-66, Table 3, 10wt% Methanol Solution in CO_2

Hydrate Thermodynamics

Detailed explanations of methods to predict hydrate formations using statistical thermodynamic techniques are presented in Sloan (1998) [8] and Parrish and Prausnitz (1972) [9] among others. As is required by equilibrium, the chemical potential of water in the hydrate phase must be equal to the chemical potential of water in remaining phases at the point of hydrate formation. Mathematically, this is represented by:

$$\mu_w^H = \mu_w^{\phi_1} = \mu_w^{\phi_2} = ... = \mu_w^{\phi_N} \quad (1)$$

In the calculation of the equilibrium criteria involving hydrates, the equilibrium is normally stated in terms of chemical potential differences as:

$$\Delta\mu_w^H = \Delta\mu_w^{\phi_i}$$
$$(i = 1,2,...,N, i \neq H) \qquad (2)$$

where $\Delta\mu_w^H$ represents the chemical potential difference of water in an empty hydrate cavity (μ_w^β) and a filled hydrate cavity (μ_w^H) and $\Delta\mu_w^{\phi_i}$ represents the chemical potential difference of water in an empty hydrate cavity and in all other phases ϕ_i ($\mu_w^{\phi_i}$):

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H \qquad (3)$$

$$\Delta\mu_w^{\phi_i} = \mu_w^\beta - \mu_w^{\phi_i} \qquad (4)$$

For the experimental measurements in this discussion, a free water phase is always present. Since by equation (1) the chemical potential difference of water in the free water phase will be

equal to that in all other phases present, we will focus solely on the calculation of the chemical potential difference in the free water phase. Therefore, the free water phase (either liquid water or ice, depending on temperature and composition) will be denoted as ϕ. (Note that a free water phase does not need to be present for hydrate formation to occur.)

Statistical thermodynamic expressions for $\Delta\mu_w^H$ can be found in Sloan (1998) and Parrish and Prausnitz (1972). These references also provide techniques to compute the value of $\Delta\mu_w^\phi$ based on classical thermodynamic derivations. Required for the computation of the chemical potential difference in equation (4) is the chemical potential of water in the free water phase ϕ. This value is provided by:

$$\mu_w^\phi = \mu_w + RT \ln a_w^\phi = \mu_w + RT \ln x_w \gamma_w \quad (5)$$

where a_w^ϕ represents the activity of water in the free water phase ϕ, μ_w represents the chemical potential of pure water, x_w is the mole fraction of water, and γ_w is the activity coefficient of water. The activity coefficient is defined as the ratio of the activity and the mole fraction of the component of interest. If free water is present as ice, $\mu_w^\phi = \mu_w$, since ice is assumed to be pure water. When inhibitors are not present and the hydrate former is relatively insoluble in water, a_w^ϕ can be assumed to be unity in equation (5) so that the chemical potential of water in the mixture of phase ϕ is that of pure water. However, when the hydrate former is relatively soluble in water or inhibitors are present, this assumption is no longer valid and the water activity must be estimated.

According to the Phase Rule, one degree of freedom exists in a binary hydrate forming system (hydrate former + water) where free water is present (either as ice or as a liquid) and the hydrate former exists in a single phase (either vapor or liquid). Therefore, if the pressure is fixed in the measurement, the hydrate forming condition will be known. The amounts of each component in a binary system do not need to be known. Further, by satisfying the equilibrium requirement of equal temperature, pressure, and chemical potentials of both components in all phases, the composition of each phase can be calculated using a flash type calculation. Obviously, during the solution of the flash, the chemical potentials of both components in all phases will be calculated including that of water defined in equation (5).

For systems involving single hydrate formers with inhibitors or multicomponent hydrate formers, the Phase Rule indicates the number of degrees of freedom will increase by the additional number of components present. For example, with a single hydrate former in a methanol inhibited measurement, the number of degrees of freedom will now be two. Therefore, for a fixed pressure, the hydrate formation temperature is no longer determined without fixing another property. Since the experimental system is closed, Duhem's theorem applies and the state of the system can be fixed by specifying the initial amount of each species. Consequently, without specification of the overall composition, a range of hydrate formation temperatures can be found at a fixed pressure by changing the overall composition. The magnitude of this range depends upon the mutual solubility of hydrate formers and inhibitors.

If the mutual solubility of the hydrate formers and the inhibitors is low, the mole fraction and activity coefficient of water in the free water phase needed in equation (5) can be estimated as a binary mixture of inhibitor and water of the composition introduced in the equilibrium cell.

In this case, the overall composition is not required to estimate the hydrate formation conditions. This is a common practice in many calculation methods. However, for higher mutual solubility, the mole fraction and activity coefficient for water can no longer be estimated in this manner due to the transfer of material between phases. In order to determine these properties, a rigorous flash calculation is necessary requiring a composition dependent model for the activity coefficient and the knowledge of the overall composition (or other Phase Rule variables).

Experimental Presentation

The hydrate formation conditions presented in the referenced GPA reports contain methanol and other inhibitors such as ethylene glycol. The methanol concentration ranges from uninhibited cases to 85 wt % concentration. It is quite evident from the data that the hydrate formation conditions are strongly influenced by the concentration of methanol. Unfortunately the overall composition of the experimental cell is not reported in any of these reports. Further, the description of the experimental procedure in these reports is normally quite terse preventing an approximation of the overall composition from being deduced.

While the hydrate forming conditions of all systems containing more than two components (including inhibitor and water) are affected by the overall composition, the lack of overall composition presentation presents a more serious problem in utilizing the data of carbon dioxide systems, and to a lesser extent H_2S, especially at higher methanol concentrations. The problem is more severe in the LLH (liquid CO_2-liquid inhibitor solution-hydrate) region of the measurements. For these cases, the mutual solubility between both liquid phases can be significant. As shown in Table 2, RR-66 indicates that with a 20 wt % methanol-water system, the concentration of CO_2 in the water-methanol rich phase is about 3.6 % (molar).

Table 2. Liquid-Liquid Equilibrium Phase Compositions for Carbon Dioxide
in a 20 Wt % Methanol-Water Solution at 27.7°F and 1342 psia
as reported in GPA RR-66, Table 13

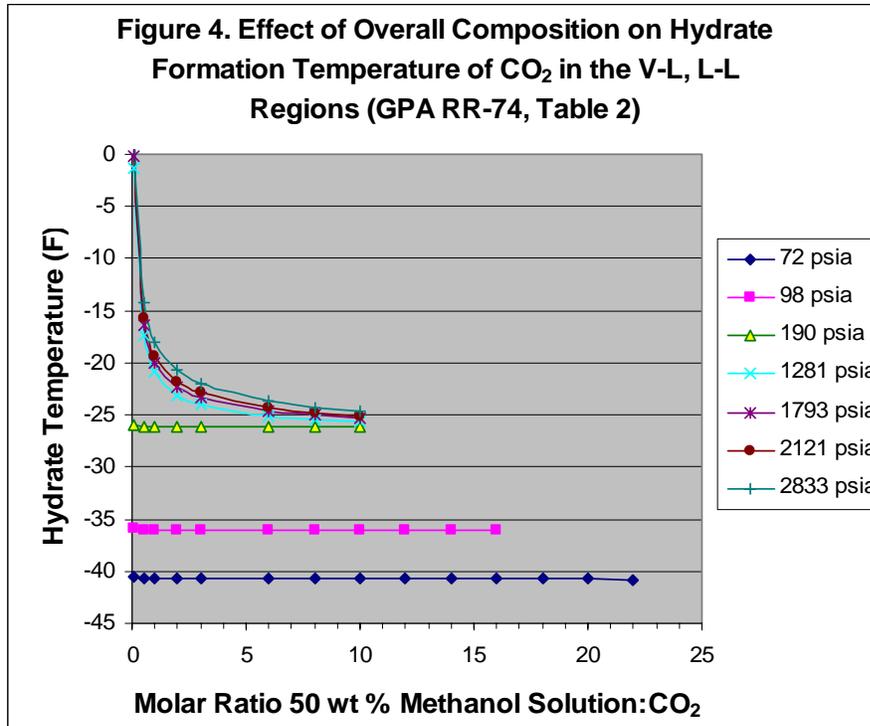| Component	Feed (mole fraction)	Aqueous Liquid	Non-Aqueous Liquid
H_2O	0.8322	0.852	0.00162
Methanol	0.1168	0.112	0.00475
CO_2	0.051	0.036	0.99363

Other data, including those of Yoon et al. (1993) [10] in Table 3, show significantly higher amounts of CO_2 in the methanol at other conditions. Further, the Yoon et al. data show the distribution of methanol and water in the liquid CO_2 rich phase can be approximately 10%. The net effect of this component distribution between the two liquid phases is a water concentration (and activity) that is significantly different from the initial inhibitor conditions. From the phase rule arguments above, the extent of this distribution depends upon the amount of CO_2 relative to the methanol-water solution charged to the apparatus. The effect on predicted hydrate formation results in a change in water chemical potential as represented by equation (5) through its impact on the water activity. The net effect on hydrate formation temperature prediction can be greater than 10°F (5°C). Considering these facts, the data for CO_2 methanol inhibited systems must be used with caution. If the overall composition is not approximately the same as the unstated experimental composition, the hydrate formation conditions can depart significantly from the reported values.

Table 3. Two and Three Phase Equilibrium Compositions for
Carbon Dioxide, Methanol and Water

Temperature (F)	Pressure (psia)	Component	Vapor	Liquid 1	Liquid 2
89.6	1044	CO_2	0.975	0.396	0.895
		Methanol	0.022	0.485	0.091
		Water	0.003	0.119	0.014
89.6	1069	CO_2	0.989	0.101	0.907
		Methanol	0.009	0.367	0.048
		Water	0.002	0.532	0.045
89.6	1087	CO_2	0.991	0.031	0.917
		Methanol	0.005	0.162	0.020
		Water	0.004	0.807	0.063
95	1109	CO_2	0.988	0.468	0.903
		Methanol	0.011	0.448	0.084
		Water	0.001	0.084	0.013
95	1025	CO_2	0.985	0.180	0.93
		Methanol	0.013	0.468	0.047
		Water	0.002	0.352	0.023
100.4	1174	CO_2	0.983	0.416	0.917
		Methanol	0.016	0.475	0.072
		Water	0.001	0.109	0.011

Any attempt to use the published hydrate formation conditions to verify process simulation predictions requires a discernment of the overall composition. RR-74 acknowledges the higher mutual solubility of CO_2 present in the methanol-water system. The report also indicates the experimental procedure was designed to ensure the overall feed composition remained unchanged during the course of the study. Again, no mention of this composition is provided. In RR-66 and RR-87, a single sample phase composition is provided near hydrate forming conditions (within 1°C) for both the vapor-liquid and liquid-liquid regions using a 10 and 20 wt % initial methanol concentration in contact with the CO_2 containing systems presented in the report. These phase compositions include the temperature and pressure along with the composition of the feed and all phases present at this single measurement. Since the reported hydrate forming conditions presented elsewhere in the report are near the hydrate forming conditions of the sample phase compositions, it is likely safe to assume that the hydrate forming conditions tabulated in these reports are approximately at the same overall composition as the stated sample phase compositions. Unfortunately, no sample phase compositions are provided for the higher methanol concentrations, the region where the mutual solubility between the phases present is much higher and the prediction significantly influenced by the overall composition. Therefore, it is difficult to verify the higher methanol concentration data in a process simulation program.

Figure 4 shows the effect of the methanol/water solution amount relative to the amount of CO_2 for a methanol concentration of 50 wt % in the vapor-liquid and liquid-liquid regions. These data points were chosen from hydrate forming conditions published in GPA RR-74, Table 2.

Figure 4. Effect of Overall Composition on Hydrate Formation Temperature of CO_2 in the V-L, L-L Regions (GPA RR-74, Table 2)
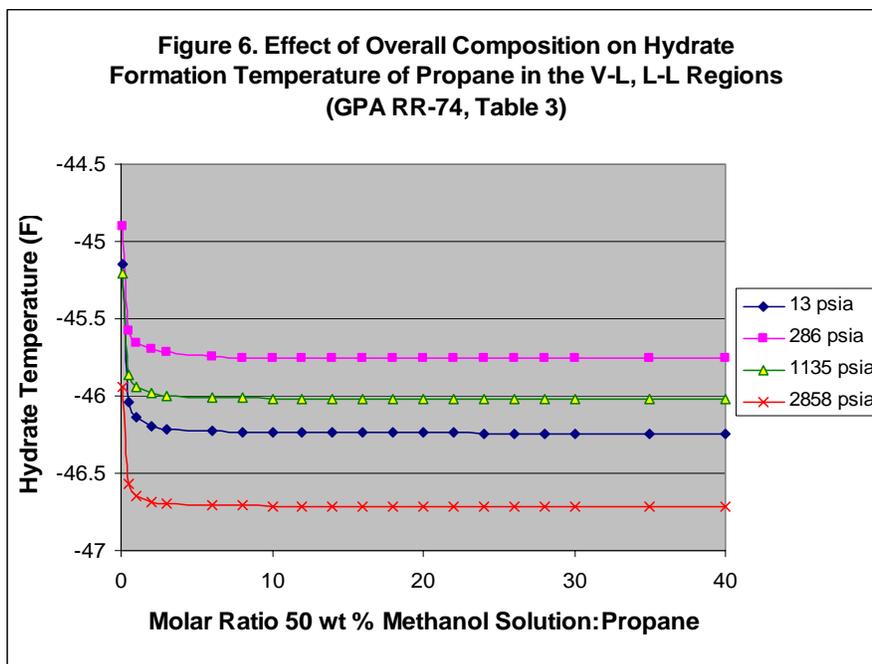
The pressures of 190 psia and below represent vapor-liquid equilibrium and the higher pressures are liquid-liquid equilibrium. At increasing amounts of methanol solution, a dramatic change in hydrate temperature predictions can occur due to the change in overall composition. Figure 5 represents a 10 wt % methanol solution for the hydrate forming conditions presented in GPA RR-66, Table 3.

Figure 5. Effect of Overall Concentration on Hydrate Formation Temperature of CO_2 in V-L, L-L Regions (GPA RR-66, Table 3)
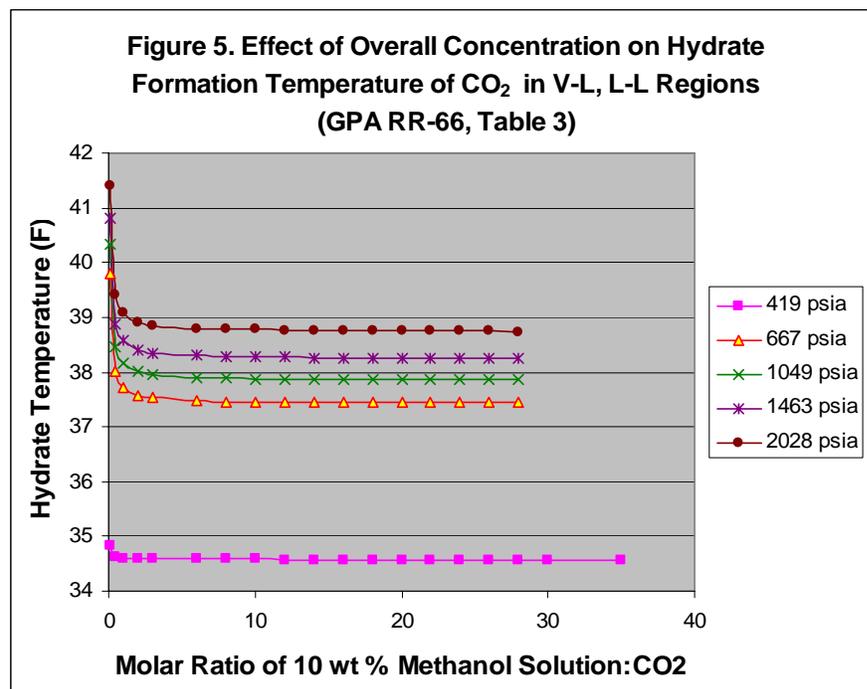
The effect on hydrate formation temperature is much less pronounced in the 10 wt % methanol solution. (Note the change in temperature scale between Figures 4 and 5.)

To further illustrate the special nature of the CO_2 systems, a hydrate temperature plot for propane in contact with a 50 wt % methanol solution is shown in Figure 6. Here the 13 psia case represents vapor-liquid conditions and the higher pressures are liquid-liquid conditions. Notice there is essentially no deviation in the hydrate prediction temperature except at very low solution ratios in the range of 0.1 to 0.5. Even at these conditions, the difference in predicted hydrate temperature is less than 1°F.

Figure 6. Effect of Overall Composition on Hydrate Formation Temperature of Propane in the V-L, L-L Regions (GPA RR-74, Table 3)

Summary and Conclusions

In this paper we have provided some of the background information required to interpret hydrate conditions. First, we note that the water content of natural gas is not significantly impacted by small amounts of acid gas at pressures below 1000 psia. Next we discuss some of the thermodynamic background necessary to calculate hydrate formation conditions. Using phase rule arguments, we state that overall compositions should be presented when publishing inhibited or multicomponent hydrate formation conditions, especially when systems exhibit high mutual solubility as in the case of carbon dioxide. Finally, we show the effect of the overall composition on hydrate forming conditions and note that special caution must be exercised when using published data for carbon dioxide systems since the experimental overall composition may not match the composition of your scenario.

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