An Analysis of Hydrate Conditions and Property Predictions in Acid Gas Injection Systems

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Abstract

This paper will focus on the hydrate formation conditions for acid gas mixtures commonly found in acid gas injection systems. Many studies have analyzed the hydrate and solid formation temperatures of CO₂ systems. However, very little is known about hydrate conditions in varying acid gas mixtures as experienced in many injection systems. Herein, the available published data will be presented and compared with predictions from the process simulation software, ProMax [®]. In particular, the hydrate conditions for both saturated and under-saturated systems will be explored for comparison on these injection systems.

Introduction

Hydrates are solid formations similar to ice. They are composed of water molecules combined with other smaller molecules such as CO_2 and H_2S .

Many studies have analyzed hydrate and solid formation temperatures of CO_2 and H_2S systems. These studies have been historically taken on as a response to interest in enhancing oil recovery through gas injection. However, the industry's interest in hydrates now grows due to stricter regulations on CO_2 emissions. CO_2 capture has now become necessary in many geographical areas. As a result, there is increasing interest in acid gas injection as a method of capturing and storing CO_2 .

As natural gas demand increases and regulations for a sweeter gas become stricter, the focus on properly handling these acid gas injection streams becomes more important. Engineers must properly predict the vapor-liquid equilibrium and the hydrate formation temperatures of these $CO_2/H_2S/H_2O$ streams to ensure operating conditions will not lead to complete or even partial hydrate formation.

The gas sweetening process typically found in sour gas plants produces a CO_2/H_2S rich gas stream. An acid gas stream is the overhead product of a solvent regeneration tower and is thus saturated with water. In preparation for injection, this stream enters a series of compressors, coolers, and knock-out drums. As an acid gas stream is compressed, cooled and fed to a knock-out drum, water is removed. As the acid gas stream is further compressed, it can then be described as under-saturated.

Unfortunately, much less is known about the vapor-liquid equilibrium and solids formation conditions of the water and acid gas in injection systems. Specifically, very few data sets are available for H₂S/CO₂ hydrate formation in under-saturated conditions. Engineers challenged with designing these injection systems typically rely on process simulation to estimate these hydrate formation conditions. Further, process simulators rely on existing data and thermodynamic equations to interpolate and extrapolate solid formation at various conditions.

This paper reviews known data sets in various acid gas conditions and compares them to the predictions given by the ProMax simulation software. Proper vapor-liquid equilibrium and property predictions will be verified first. Then hydrate predictions can be compared to those experimentally determined in trusted data sets. These trusted data sets all occur in saturated conditions. Once simulations are trusted with hydrate conditions, we can then review hydrate temperature predictions in undersaturated conditions and compare to a single data set.

First vapor-liquid equilibrium data sets and molar densities for CO₂, H₂S, and CO₂/H₂S systems will be compared to simulation results. Next, experimentally determined hydrate temperatures will be compared to simulation result for CO₂, H₂S, and CO₂/H₂S systems. Finally, predictions of injection acid gas systems in under-saturated conditions will be reviewed and benchmarked against experimental data.

Vapor-Liquid-Equilibrium

Proper determination and interpretation of hydrate formation boundaries requires understanding of the vapor-liquid equilibrium and the variables which can affect their boundaries. Certainly, composition, temperature, and pressure of a system play an important role in vapor-liquid equilibrium and hydrate formation. Moreover, the effect of composition on hydrate potential is magnified as the operating pressure increases. At pressures found in acid gas injection systems, simple gas gravity correlations to determine water content must be abandoned for experimental data or more rigorous VLE calculations. Therefore, any simulation predictions must be compared to trusted data sets of vapor-liquid equilibrium for general agreement.

Presented in Figure 1 is a graph displaying the water content, in grams of H_20 per m³, of a CO₂ system at varying temperatures as a function of pressure. Data from GPA report RR-99[1] at 25° C are plotted along with simulation predications at various temperatures. This graph is similar in design to that provided by Strickland [2] and includes the minimum water content line at 43° C condition. The purpose of this graph is to verify that composition predictions agree with published and trusted data.





Obviously, pressure and temperature both influence the composition of a gas stream. The 43° C line contains a trough near70 bar. The bottom of this trough represents the minimum amount of water the CO₂ gas can hold at 43° C at that corresponding pressure. As Strickland pointed out, much of the water can be removed at the trough of the curve during the first or second compression stage of injection systems through a knock-out drum. Once the water is dropped out in a knock-out drum, any increase in pressure will result in under-saturated conditions at that same temperature.

Figure 2 is an equivalent graph considering an H_2S and H_2O only system. Again, ProMax results at varying temperatures are plotted along with results from GPA RR-48[3] at 37.8° C. A minimum water content line is also included for the system at 43° C.



Fig. 2. Water Content for H₂S-Rich Phase vs Pressure

Figure 2 shows that water content of H_2S gas systems is more sensitive to pressure in the range of 0 to 50 bar than that of the CO₂ gas systems. The H_2S system in this case does not show a smooth trough but rather a "cliff." This "cliff" signifies a phase change.

In further consideration of vapor-liquid equilibrium, the interplay of various H_2S and CO_2 gas compositions must be reviewed and data should be diligently compared to simulation results. Huang[4] presented VLE of two different compositions under various temperatures and pressures. Tables 1 and 2 contain portions of the data presented by Huang. Table 1 displays the phase behavior in a stream of 15% CH₄, 30% CO₂, 5% H₂S, and 50% water on a molar basis. Phase data were collected at 37.8° C and at varying pressures. Table 2 displays the same data at a composition of 5% CH₄, 5% CO₂, 40% H₂S, and 50% water on a molar basis. The simulation results are listed beside for comparison.

	Table 1.							
Huar	Huang, S., Leu, AG., Ng, HJ., and Robinson, D.B., "The Phase Behavior of Methane, Carbon							
DI	Dioxide, Hydrogen Sulfide, and Water," Fluid Phase Equilibria, 19, 21-32 (1985), Table 1							
	Temperature	37 8000	۹C	Comp	onents	Mole Percent		
		37.8880	-0					
	Pressure	4.8200	МРа	$\Box CH_4/CO_2/H_2$	S/H ₂ O	15/30/5/50		
	Experin	nental data		с	alculated by P	roMax		
	Total	Vapor	Light Liq	Total	Vapor	Light Liq		
CH₄	0.1494	0.3040	2.76E-04	0.1494	0.3023	3.01E-04		
CO ₂	0.3005	0.5945	9.30E-03	0.3005	0.5993	9.05E-03		
H ₂ S	0.0497	0.0998	5.03E-03	0.0497	0.0964	4.19E-03		
H ₂ O	0.5004	1.91E-03	0.9854	0.5004	2.03E-03	0.9865		
	Pressure	7.6	MPa]				
CH_4	0.1488	0.3031	4.66E-04	0.1494	0.3039	4.84E-04		
CO ₂	0.2991	0.5970	0.0121	0.3005	0.5989	0.0124		
H_2S	0.0494	0.0982	5.40E-03	0.0497	0.0954	5.40E-03		
H_2O	0.5027	1.71E-03	0.9816	0.5004	1.70E-03	0.9817		
CH_4	0.1488	0.3031	4.66E-04	0.1494	0.3039	4.84E-04		
	Pressure	12.52	MPa					
CH_4	0.1497	0.30 ₂ 9	7.96E-04	0.1494	0.3044	8.13E-04		
CO ₂	0.3010	0.5967	0.0151	0.3005	0.5982	0.0150		
H_2S	0.04980	0.0985	5.95E-03	0.0497	0.0955	5.83E-03		
H ₂ O	0.5000	1.87E-03	0.9781	0.5004	1.87E-03	0.9784		
	Pressure	16.93	MPa					
CH_4	0.1495	0.3021	9.90E-04	0.1494	0.3044	1.07E-03		
CO ₂	0.3006	0.5963	0.0154	0.3005	0.5978	0.0157		
H_2S	0.0497	0.0996	6.08E-03	0.0497	0.0956	5.66E-03		
H ₂ O	0.5002	1.99E-03	0.9777	0.5004	2.19E-03	0.9775		

Table 2.
Huang, S., Leu, AG., Ng, HJ., and Robinson, D.B., "The Phase Behavior of Methane,
Carbon Dioxide, Hydrogen Sulfide, and Water," Fluid Phase Equilibria, 19, 21-32 (1985),
Table 2

	Temperature	107.2	°C	Components CH ₄ /CO ₂ /H ₂ S/H ₂ O		Mole Percent 5/5/40/50	
	Pressure	7.56	MPa				
	Experimental data			<u>C</u>	Calculated by ProMax		
	Total	Vapor	Light Liq	Total	Vapor	Light Liq	
CH_4	0.0494	0.1182	1.55E-04	0.0494	0.097679	1.69E-04	
CO_2	0.0493	0.1112	1.25E-03	0.0493	0.096305	1.37E-03	
H_2S	0.4072	0.7485	0.0304	0.4072	0.777303	0.029796	
H_2O	0.4941	0.0253	0.9682	0.4941	0.028714	0.968667	
	Pressure	12.27	MPa				
CH_4	0.049805	0.106	3.32E-04	0.049805	0.100292	3.64E-04	
CO_2	0.049605	0.1148	2.26E-03	0.049605	0.097926	2.29E-03	
H_2S	0.40194	0.7528	0.0361	0.40194	0.772837	0.038729	
H_2O	0.49865	0.0264	0.9613	0.49865	0.028945	0.958621	
	Pressure	16.92	MPa]			
CH_4	0.0499	0.1207	6.06E-04	0.0499	0.099885	6.14E-04	
CO ₂	0.0498	0.1176	3.34E-03	0.0498	0.097251	3.01E-03	
H₂S	0.4009	0.7322	0.0392	0.4009	0.766627	0.040287	
H_2O	0.4994	0.0295	0.9568	0.4994	0.036236	0.956086	

From a sampling of these VLE data, water content is calculated on a lbm $H_2O/MMSCF$ basis, and plotted along with simulation results in Figures 3 and 4. Note the dramatic roles temperature, pressure, and composition play on vapor-liquid equilibrium. It should be noted that simulation results closely match experimental data.



Fig. 3. Water Content vs Pressure for a Mixture of $CH_4/CO_2/H_2S/H_2O$ with 15/30/5/50 % mol



Fig. 4. Water Content vs Pressure for a Mixture of $CH_4/CO_2/H_2S/H_2O$ with 5/5/40/50 % mol

While the data sets represented in Figures 3 and 4 may not reflect the realistic compositions of an acid gas injection stream, it is important that simulations thermodynamically match trusted data sets. It has now been shown that ProMax is accurately simulating the known VLE data sets. The same thermodynamic principles utilized thus far will be relied upon to simulate in regions where little data have been published.

Property Predictions - Molar Densities

In consideration of equipment design, thermodynamic property predictions from simulation should be considered also. The varying densities and static head may have tremendous influence on compressor sizing calculations. Experimental data of the molar density of a H₂S/CO₂ rich stream will be analyzed and compared to simulation predictions.

Table 3 represents data from GPA RR-174[9] and reports experimental densities at varying pressures and H_2S/CO_2 molar ratios. These compositions combined with 5% methane mirror many injection system conditions. ProMax results are inserted next to the experimental results for comparison.

Table 3						
GPA RR-174 Tables 5 & 11						
Tempera	Temperature = 120 PF Density H ₂ S/CO ₂					
		rich phase				
	H ₂ S/CO ₂	<u>RR-174</u>	ProMax			
<u>P /psia</u>	<u>mole ratio</u>	<u>g/cm3</u>	<u>g/cm3</u>			
200	1:3	0.023	0.0220			
1500	1:3	*0.178*	0.3561			
4000	1:3	0.776	0.7964			
10000	1:3	0.920	0.9883			
200	1:1	0.021	0.0210			
1500	1:1	0.581	0.5679			
3000	1:1	0.720	0.7418			
5000	1:1	0.787	0.8350			

Simulation utilized a modified Peng-Robinson equation of state for calculation of density. This equation of state produces very good approximations for near and above critical conditions. The Peng-Robinson method therefore proves to be of value when approaching critical conditions. The data point for 1500psia at the 1:3 molar ratio is of suspect quality as several different calculation methods agreed on the calculated density of reported at 0.3561 g/cm3. Figures 5 and 6 graphically represent the information in Table 3.







Stouffer 2001 [10] also presented data regarding molar density at various pressures and temperatures. The data again focus on a rich acid gas stream similar to injection systems. A Peng-Robinson equation of state was utilized for calculation/prediction of the densities through simulation. Figure 7 displays the Stouffer data along with simulation results.



Fig. 7. Pressure vs. Molar Density for a mixture of 50.01 mol % of CO2

Simulation results utilizing the Peng-Robinson equations of state for density calculations follow very closely to experimental results up to pressures of 18MPa.

Saturated CO₂ Hydrates

With confidence that simulation VLE and density calculations matches trusted experimental data sets, the hydrate formation points should subsequently be reviewed for general agreement between published datasets and simulation or calculation methods.

Figure 8 displays the data points of several different sources which experimentally measured hydrate points in the three phase region of CO_2/H_2O systems [5]. Simulation results of those same conditions are also plotted for comparison. Notice the general agreement.



Fig. 8. Three Phase Hydrate Data for CO₂ Hydrates

At a given pressure, as temperature is dropped from the right side of the graph to the left, there are two potential hydrate formation temperatures in the pressure range of 1000 to 4000 kPa. Also note high pressures of approximately 5000 kPa to 10000 kPa have little influence on the hydrate formation temperatures. This is due to the relative incompressibility of liquids and can be seen by reviewing the Lw-H-LCO₂ curve above on Figure 5. This curve is verified by the Ng[9] data points, also plotted on Figure 8.

The potential effect of a light hydrocarbon such as methane should also be considered. Table 4 lists results as presented by Fan[6] for a $CH_4/CO_2/H_2O$ system along with simulation results. The table is then plotted for easier comparison in Figure 6.

Table 4.							
F	Fan and Guo (1999) Lw-H-V						
	Components Mole Percent						
	3.46/96.54						
	Experimental	<u>ProMax</u>					
р	T exp / K	Tcal /K					
/kPa							
1100	273.5	272.0					
1160	273.6	272.5					
1200	273.7	272.8					
1950	277.2	277.2					
1940	277.6	277.1					
2050	277.9	277.6					
3000	280.4	280.8					
3730	281.7	282.4					
4800	282.3	284.0					





Table 4 and Figure 9 represent only the Lw-H-V hydrate points. There are many more data sets of similar type and of different loci which will not be analyzed or compared in this paper.

It has now been shown the ProMax simulation results closely mirror experimental hydrate data for CO₂ three phase systems at varying temperatures, pressures, and compositions.

Saturated H₂S Hydrates

Just as was done with the CO₂ system, known and trusted H₂S hydrate data sets must be analyzed and compared to simulation results.

Figure 10 is a plot of H_2S hydrate points for a H_2S/H_2O three phase system. Again, several sources are plotted along with simulation results[5]. The Lw-H-LH₂S locus and Selleck data demonstrate pressure's minor influence on hydrate temperatures at above 2000 kPa, again due to the relative incompressibility of liquids



Fig 10. Three Phase Hydrate for H₂S

Table 5 is data as presented by Selleck[7] and considers the specific region of 50-250 bar of a saturated H2S stream. The simulation results are presented for comparison.

Table 5.							
Selleck,	Selleck, F.T., Carmichael L. T., Sage B. H., Ind.						
	Eng. Chem., 44, 2219(1952)						
Experimental ProMax							
P /bar	T exp / C	Tcal /C					
34.47	29.65	29.48					
68.95	29.95	29.75					
78.26	30.05	29.83					
103.42	30.25	30.01					
137.9	30.55	30.24					
141.9	30.55	30.27					
172.37	30.85	30.47					
206.85	31.15	30.71					
209.54	31.15	30.74					
241.32	31.45	30.93					





With the presentation of Table 5 and Figure 11, it is shown that simulation results follow closely to that of trusted data sets for H_2S systems hydrate temperatures.

Thus far, vapor-liquid equilibrium data, pure component three phase hydrates, and hydrate formation of two and three component systems have been analyzed and compared to simulation results. Simulation results follow those data sets closely.

Saturated CO₂/H₂S Hydrates

Comparison of acid gas systems containing both CO_2 and H_2S is necessary at this point. Even though calculations or simulation results may match closely with a single acid gas system, the combination of these acid gases may be grossly missed if not properly reviewed.

Most published data sets revolves around acid gas systems that contain large portions of a light hydrocarbon such as methane, as is the case with Sun[8]. One hydrate data set from Sun of a CO_2/H_2S acid gas with methane is shown in Table 6 [8]. The CH₄ composition is 66.38% mol, and is at a higher concentration than what would be expected of acid gas injection systems. However, the pressures range includes those seen in injection systems. The experimental data sets are given along with the simulation results and then graphed in Figure 12. Notice again the agreement between experimental data and simulation results.

Table 6. CY Sun M6						
Composition Mole Percent			Experimental		<u>ProMax</u>	
$\% CH_4$	% CO ₂	$\% H_2S$	P in kPa	T in K	T-Hyd /K	
66.38	7.00	26.62	582.00	281.20	277.90	
66.38	7.00	26.62	786.00	284.20	280.88	
66.38	7.00	26.62	1160.00	287.20	284.71	
66.38	7.00	26.62	1788.00	290.20	288.83	
66.38	7.00	26.62	2688.00	293.20	292.49	
66.38	7.00	26.62	3910.00	295.20	295.57	
66.38	7.00	26.62	5030.00	296.70	297.39	
66.38	7.00	26.62	6562.00	298.20	299.03	
66.38	7.00	26.62	8080.00	299.70	300.07	



It has now been shown that simulation results closely agree with experimental data for hydrate temperatures of $CO_2/H_2S/CH_4$ systems. Further, this data set is at pressures comparable to acid gas injection systems.

Under-saturated Systems

As stated in the introduction, several operating conditions of acid gas injection systems are in undersaturated conditions. However, very little experimental data have been published and presented for these conditions. What little data that are published are of suspect quality as will be shown. ProMax VLE and hydrate calculation methods are not adjusted in these operating regions to fit data. Rather, the methodology used in the previous saturated conditions are continued here. Below in Tables 7 and 8 are data sets presented by Song[9] for hydrate formation temperatures of CO_2 systems at varying pressures. These tables also contains ProMax simulation results. Figures 13 and 14 represent Tables 7 and 8 respectively.

Table. 7 Song, K. Y. and Kobayashi, R., "Water Content of CO ₂ in Equilibrium with Liquid Water and/or Hydrates, SPE Formation Evaluation, 2(4), 500- 508 (1987)						
<u>Pressure</u>	<u>y-H₂O</u>	<u>Experimental</u>	<u>ProMax</u>			
P /psia	* 1000	THyd /F	THyd /F			
100	0.1800	-6.52	-2.04			
100	0.2190	-2.20	1.52			
100	0.5570	17.60	20.05			
200	0.1142	-0.40	2.06			
200	0.1471	4.67	6.81			
200	0.2201	12.20	14.58			
200	0.4885	28.40	30.73			
300	0.2775	32.00	26.37			
300	0.4368	36.50	36.04			
300	0.2321	24.25	22.66			
300	0.1194	9.50	9.34			
300	0.0890	3.20	3.67			
300	0.2013	-4.90	-1.05			
300	0.1361	-18.40	-1.05			

Table. 8 Song, K. Y. and Kobayashi, R., "Water Content of							
CO2 in Equilibrium with Liquid Water and/or Hydrates, SPE Formation Evaluation, 2(4), 500-508							
(1987)							
<u>Pressure</u>	<u>y-H₂O</u>	Experimental	<u>ProMax</u>				
P /psia	* 1000	THyd /F	THyd /F				
700	0.3313	0.04	-33.92				
700	0.4705	14.00	-20.17				
700	0.5402	25.70	-14.55				
700	0.7182	37.40	-2.56				
900	0.5170	3.20	-16.70				
900	0.6647	15.00	-6.32				
900	1.0960	44.60	15.73				
1200	1.0890	1.40	14.54				
1200	1.5741	19.00	31.80				
1200	1.8695	26.60	40.33				
1500	1.2738	1.40	20.87				
1500	1.6509	15.80	33.00				
1500	2.4687	37.40	52.41				
2000	1.5091	-0.04	27.44				
2000	1.8057	8.50	35.80				
2000	2.2043	22.20	45.35				
2000	2.7441	36.90	53.05				

Fig. 13. Hydrate Formation Temperature for CO₂ Undersaturated (V-H)



Figure 13 shows very good agreement between simulation results and experimental data. Simulation results for the 200 and 300 psia V-H line predicts temperatures slightly over experimental data. However, simulation results at 100 psia is slightly under experimental data.



In Figure 14, ProMax results grossly disagree with experimental data. However, the pressure influence on hydrate temperatures as shown by the experimental data is very interesting. Experimental data suggest that pressure greatly impacts hydrate temperatures in this LCO₂-H region. However, Figures 5 and 7 both demonstrated that pressure has very little influence on the hydrate temperatures in the LCO₂-H region. As a result, ProMax predictions show hydrate lines very close to each other for the different pressures. Unquestionably, more experimental data is required in this region.

While no reliable data exists, the results from ProMax should be extendable into the under-saturated region since the results are based on sound thermodynamic principles.

Conclusions

This paper has reviewed a wide array of conditions to ensure the ProMax simulation software's ability to determine hydrate points is built from solid foundations. By comparison to experimental data, the vapor-liquid equilibrium was shown to be accurately predicted under varying conditions by simulation as well as important property predictions. Then hydrate predictions in a variety of saturated systems were shown to agree with known and trusted published data sets.

Under-saturated experimental data sets of hydrate predictions were critically analyzed against simulation results. The critical analysis concluded the data must be supplemented with additional experimental results. However, holding to sound thermodynamic principles, ProMax should extend into these regions for hydrate calculations.

Engineers are increasing relying on simulation software for hydrate predictions in acid gas injection systems. This paper sufficiently proves that ProMax can be trusted to provide accurate results for these CO₂/H₂S under-saturated systems.

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