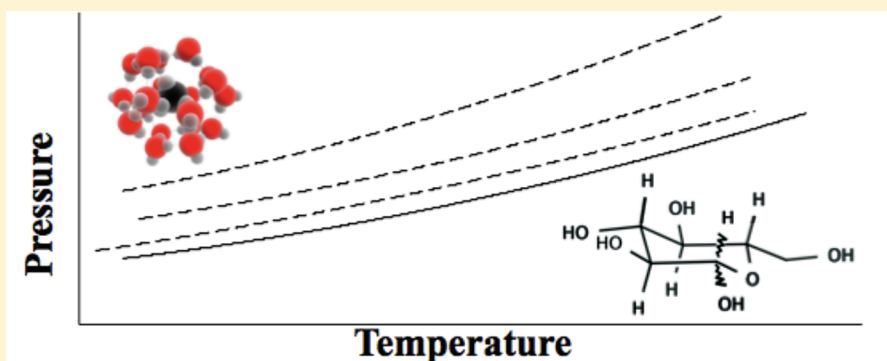# H−L$_w$−V Equilibrium Measurements of Pure Methane Gas in the Presence of D-(+)-Glucose

Anthony S. Carbone, Jason R. Ivall, and Phillip D. Servio*

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, H3A 2B2, Canada

ABSTRACT: The three-phase hydrate−liquid−vapor (H−L$_w$−V) equilibrium conditions of the methane clathrate hydrate in aqueous solutions of D-(+)-glucose were experimentally determined. Equilibrium curves were generated via an isothermal pressure-search method for systems containing (10 to 30) wt % glucose at temperatures between (275.15 and 281.25) K and with pressures ranging from (3.4 to 8.0) MPa. Experimental results show that glucose-containing systems exhibit a considerable inhibiting effect on methane hydrate equilibrium conditions, as the phase equilibria conditions for these systems are shifted to higher pressures than those for pure water systems at a given temperature. It was also found that the degree of inhibition increases in relation to the concentration of the glucose additive and that the inhibition of 30 wt % solutions of glucose is superior to low concentrations of methanol and to equal concentrations of magnesium sulfate.

1. INTRODUCTION

Gas hydrates are nonstoichiometric crystalline solids formed by water molecules in the presence of a gas or volatile liquid at high pressures and low temperatures. Under these conditions, the water molecules link together through hydrogen bonding to produce a cage-like structure that encompasses the guest molecule. The hydrate structure is thermodynamically stabilized through physical bonding between the guest and host molecules via weak van der Waals forces.[1] Gas hydrates predominantly assemble into three distinct crystal structures: structure I (sI), structure II (sII), and structure H (sH), based on the size of the guest molecule.[2]

Hydrates occur naturally around the world below the permafrost zone and in subsea sediments, and they are composed mostly of methane (which forms an s1 hydrate).[3] Estimates predict that global hydrate reserves contain more than twice as much organic carbon than the total amount of current global fossil fuel reserves,[4] which makes them a potentially colossal source of energy for the future. However, industrial interest in gas hydrates spurred in the 1930s when it was discovered that the conditions within oil and gas pipelines during extraction and transport are conducive to gas hydrate formation.[5] Hydrate agglomeration creates blockages that impede flow and damage the surrounding infrastructure. Consequently, the bulk of current hydrate research is focused on the development of chemical, thermal, mechanical, and hydraulic inhibitors to improve flow assurance.[6]

Chemical inhibition is achieved through the use of either low-dosage hydrate inhibitors (LDHI) or thermodynamic inhibitors (TI). LDHIs do not prevent hydrate formation; they merely interfere with the nucleation, growth, and agglomeration of the hydrate particles,[7,8] which is why they are further classified as either antiagglomerants (AA) or kinetic hydrate inhibitors (KHI) based on their mechanism of action.[9] The hydrate equilibrium conditions (H−L$_w$−V) are unaffected. Research into LDHI is a relatively recent yet fast-growing field, as it represents a low-dosage (0.1 to 1.0 wt %), economic solution for hydrate inhibition.[9] Thermodynamic inhibitors (TI) disrupt the stability of the hydrate network by competing for the hydrogen bonding with the water molecules. This causes the hydrate equilibrium conditions to shift in a manner that requires either lower temperatures or higher pressures to form the hydrate.[7] The degree of inhibition is directly related to the concentration of inhibitor, and it is this control that makes TI the virtually universal practice for hydrate plug prevention, with methanol and monoethylene glycol (MEG) being the most extensively used agents.[7] Unfortunately, these additives are required in massive

quantities—(10 to 50) wt % of the water phase[9]—and are not fully recovered, with some inevitably being lost to the environment.[10] These concerns are driving research into finding and developing more cost-effective and eco-friendly inhibitors.

The efficiency of methanol and ethylene glycol as TIs lies primarily in their hydroxyl group. Its high polarity allows for excellent hydrogen bond interactions, resulting in an affinity for water sufficient to break apart the hydrate crystal lattice. Furthermore, the most promising LDHIs also exhibit a polar headgroup that interacts with the water in the cage network.[9] Many studies have been conducted on the effects of aqueous solutions of alcohols, electrolytes, and polymers (or mixtures of these agents) on hydrate phase equilibrium,[11,12] but few to date have examined the effects of one of the most hydroxylated class of chemicals: carbohydrates. As ubiquitous and naturally occurring organic compounds, sugars could present an economically viable and environmentally friendly TI alternative to the current industrial TIs.

In this study, three-phase (H−L$_w$−V) equilibrium data were obtained for the CH$_4$−H$_2$O structure 1 hydrate system in the presence of D-(+)-glucose (dextrose) at concentrations from (10 to 30) wt % of the water phase. Pressures ranged from (3.4 to 8.0) MPa, and temperatures were between (275.15 and 281.25) K. As one of the most fundamental and abundant saccharides in nature, glucose is a readily available, cheap to produce, water-soluble chemical (Figure 1). It was shown to act
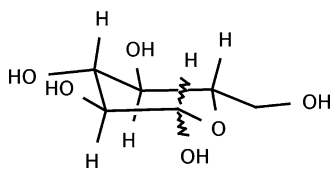

Figure 1. Molecular structure of D-(+)-glucose.

as an effective thermodynamic hydrate inhibitor at concentrations of (20 and 40) wt % for the R22 (CHClF$_2$) and for the CO$_2$ structure-1 hydrate systems at pressures ranging from (0.15 to 4.0) MPa and temperatures between (274 and 290) K.[11,12] Bond and Russell also reported phase equilibria data for 50 wt % solutions of dextrose and the structure-1 hydrogen sulfide hydrate.[11] However, to the best of our knowledge, no data have yet been published using glucose as a thermodynamic inhibitor in high-pressure, pure methane hydrate systems, which could form the basis for industrial applications.

2. EXPERIMENTAL APPARATUS

All experiments were carried out in a Jefri-DBR phase behavior system (Oilphase-DBR, Schlumberger), as used by Beltran et al. (Figure 2).[13,14] The system contains a high-pressure *PVT* cell built with a 20 cm tall glass cylinder (150 cm^3 void volume) secured between two full-length viewing windows, inside a stainless steel frame. The full-length viewing windows allow for the constant monitoring of the contents of the reactor. An automated, high-pressure, positive displacement pump (Oilphase-DBR, Schlumberger) was used to regulate the experimental pressure inside the reactor.[13] The fluid inside the pump comes into contact with a floating stainless steel piston, which isolates the hydraulic fluid from the process side of the cell. This allows the piston to exert pressure on the experimental contents without contaminating the process side with the pump fluid. The high-pressure *PVT* cell is mounted inside a temperature-regulated
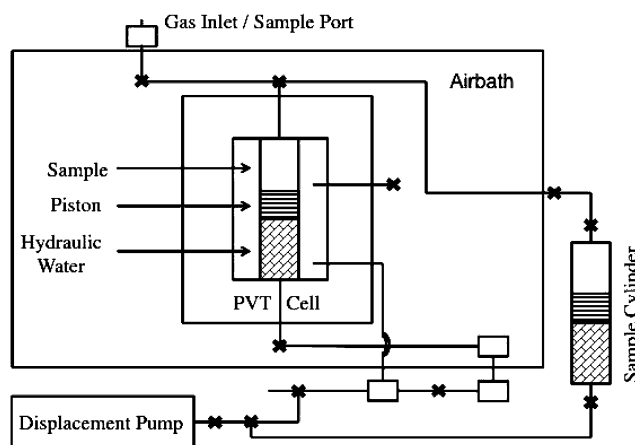

Figure 2. Jefri-DBR phase behavior system.[14]

air bath by a bracket and horizontal shaft, attached to an electric motor. The motor powers the shaft, allowing the cell to oscillate through 60° about its center of gravity, at a rate of 40 oscillation cycles per minute.[13]

The pressure and temperature inside the high-pressure *PVT* cell were monitored using a platinum RTD probe and a pressure transducer (both supplied with the phase behavior system). Using a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.2$ K and $U_P = 0.014$ MPa, for temperature and pressure, respectively.[13]

3. EXPERIMENTAL PROCEDURE

The process side of the *PVT* cell was loaded with 30 cm^3 of 0 wt %, 10 wt %, 20 wt %, and 30 wt % glucose solution. These solutions were prepared using a Denver Instrument S-4002 top loading scale. The D-(+)-glucose used was provided by Sigma-Aldrich Canada Ltd. with a purity rating of ≥ 99.5 % (GC). UHP CH$_4$ gas provided by MEGS Specialty Gases was brought into contact with the glucose mixture, then pressurized to a value just below the expected hydrate forming region, and left overnight to saturate and equilibrate.[13] Agitation of the *PVT* cell began once all of the necessary chemicals were loaded into it. To induce hydrate crystallization, the positive displacement pump was used to move the isolation piston forward, thus increasing the pressure of the system above the equilibrium value for pure water. Once hydrates were formed, the system was allowed to equilibrate (at least 2.5 h), and pressure, temperature, system volume, and hydrate presence in the bulk were monitored. The liquid (aqueous) + hydrate + gas equilibrium conditions were measured using the isothermal pressure search method.[15−17] This pressure search technique satisfies the phase rule[18] for the system described in this paper. The system's pressure was decreased in steps of 0.05 MPa, allowing for the cell's temperature to equilibrate between each pressure decrease. To decrease the pressure in the cell, the positive displacement pump was used to retract the isolation piston located within the *PVT* cell. Care was taken to avoid large temperature fluctuations, maintaining the cell temperature within ± 0.4 K of the original value for at least 60 min before carrying out the next pressure decrease. As carried out by Beltran et al.,[13] this procedure was repeated until visual confirmation of hydrate disappearance was achieved; the equilibrium temperature and pressure conditions were then taken as the mean of the conditions at

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which the final hydrate crystal was observed and the conditions at which the final hydrate crystal disappeared.

The estimated standard uncertainties were as follows: for temperature $u_T = 0.2$ K, for pressure $u_P = 0.03$ MPa. Since the coverage factor used is $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.4$ K and $U_P = 0.06$ MPa.[13] Experiments were not conducted for aqueous solutions containing greater than 30 wt % glucose since the maximum solubility of glucose in pure water within the temperature range used is ca. 40 wt % glucose.[19] To prevent glucose crystallization in the PVT cell, a 30 wt % glucose aqueous solution was used as an upper boundary for data acquisition.

4. RESULTS AND DISCUSSION

The effects of aqueous solutions of D-(+)-glucose on methane hydrate phase equilibria conditions were determined via the isothermal pressure-search method. The experimental three-phase (H−L$_w$−V) equilibrium temperature and pressure measurements are tabulated in Table 1 based on glucose composition,

Table 1. Phase Equilibrium Data for Systems Containing (0 to 30) wt % Glucose

system	T/K	p/MPa
methane + water (0 wt % glucose)	275.8	3.35
	277.4	3.98
	279.5	4.85
	281.1	5.81
methane + water + 10 wt % glucose	275.4	3.43
	275.5	3.48
	277.3	4.23
	279.5	5.12
	280.9	5.87
	281.3	6.02
methane + water + 20 wt % glucose	275.3	3.81
	275.4	3.85
	277.3	4.71
	279.2	5.67
	280.9	6.61
	280.9	6.60
methane + water + 30 wt % glucose	275.2	4.43
	275.3	4.43
	277.4	5.46
	279.3	6.65
	280.8	7.74
	280.9	7.77

and the corresponding three-phase equilibrium curves are illustrated in Figure 3. Note that the trendlines for each system are inserted merely as a visual aid and are not modeled after a particular regression type. The accuracy of the data acquired using the previously described equipment was verified by comparison of pure water (0 wt % glucose) results with data published by Deaton and Frost[20] for an equivalent system within the same temperature range. These results were found to lie within the experimental uncertainty of the work presented by Deaton and Frost, and they are used as a baseline to establish the inhibition effect of the glucose solutions tested in this study (Figure 3). Note that an inhibition effect is observed when hydrate equilibrium conditions are shifted to higher pressures and/or lower temperatures due to the presence of the chemical additive.[21]
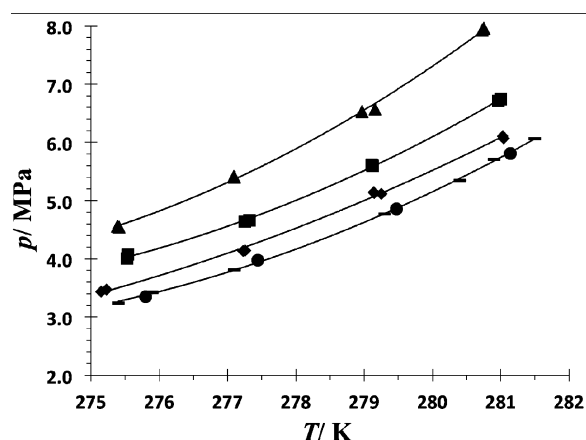

Figure 3. Measured phase equilibrium conditions of the water + glucose + methane system (●, 0 wt % glucose, this work; —, 0 wt % glucose, Deaton and Frost, 1946;[20] ◆, 10 wt % glucose; ■, 20 wt % glucose; ▲, 30 wt % glucose).

Figure 3 demonstrates that glucose-containing systems exert an inhibitive effect on methane hydrate systems as the phase equilibrium conditions are shifted above the pure water baseline values for a given temperature. The degree of inhibition increases in relation to the concentration in what appears to be an exponential manner, and this effect is most pronounced at the 30 wt % composition where, on average, 37 % more pressure is required at a given temperature to reach hydrate-forming conditions. Figure 4 then compares the performance of the 20 wt %
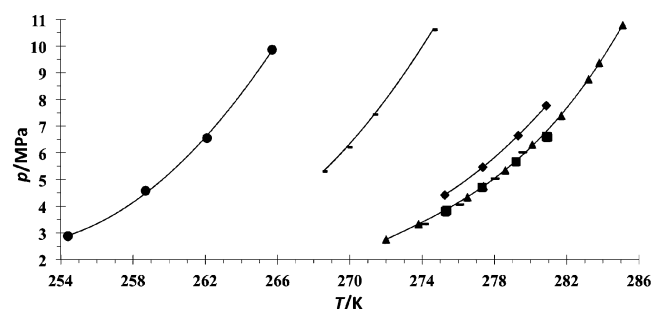

Figure 4. Measured phase equilibrium conditions of the water + glucose + methane system (◆, 30 wt % glucose; ■, 20 wt % glucose, this work); reported equilibrium conditions of the water + methanol + methane system (●, 35 wt % methanol; ▲, 4.2 wt % methanol);[21] reported equilibrium conditions of the water + MEG + methane system (-, 35 wt % MEG);[21] reported equilibrium conditions of the water + MgSO$_4$ + methane system (—, 28 wt % MgSO$_4$).[22]

and 30 wt % glucose systems to published values for systems containing methanol and MEG, which are commonly used TIs, and magnesium sulfate (MgSO$_4$), a salt.[21,22] Although the 30 wt % glucose mass fraction is vastly outclassed by 35 wt % solutions of either methanol or MEG, its performance is markedly better than systems containing either 4.2 wt % methanol or 28 wt % MgSO$_4$. Furthermore, 20 wt % glucose mixtures exhibit a nearly equivalent effect as the 4.2 wt % methanol or the 28 wt % MgSO$_4$ systems.

5. CONCLUSIONS

Three-phase (H−L$_w$−V) methane hydrate phase equilibrium conditions were established for systems containing aqueous solutions of D-(+)-glucose. A significant inhibiting effect was observed

for glucose fractions between 0.1 and 0.3 of the water phase, with the inhibitive strength increasing in relation to the concentration of additive. Furthermore, the performance of 20 wt % glucose was analogous to that of 4.2 wt % methanol and 28 wt % $MgSO_4$. These findings suggest that glucose could be an environmentally friendly substitute to operations which require low degrees of thermodynamic inhibition.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +1-514-398-1026. Fax: +1-514-398-6678. E-mail: phillip.servio@mcgill.ca.

Notes

The authors declare no competing financial interest.

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(18) The degrees of freedom for this system are calculated using the following phase rule formula: $F = C − p + 2$, where F is the system's degrees of freedom, C are the number of components present in the system, and p denotes the number of phases present in the system. In this specific case, $C = 3$ (water, glucose, methane) and $p = 3$ (vapor, liquid, solid). We are left with the degrees of freedom equal to 2. Therefore, three properties of the system must be reported; these were temperature, pressure, and glucose mass fraction. This results in a fixed equilibrium pressure that is found using the isothermal pressure search method.

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